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Effect of chemical admixtures on properties of alkali-activated Class C fly ash

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Effect of chemical admixtures on properties of alkali-activated Class C fly ash

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Abstract

Effect of chemical admixtures on properties of alkali-activated Class C fly ash

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Geopolymers are considered an alternative to portland cement in the construction industry since they can be formulated to possess comparable performance. Geopolymers are synthesized by alkaline activation of aluminosilicate materials. In this study, three sources of high calcium, Class C fly ash were used as the aluminosilicate sources for geopolymer synthesis. One major problem of high-calcium fly ash geopolymers is the workability. The goal of this work was to find a way to improve the workability of geopolymer pastes. The workability of the geopolymer pastes was assessed by the mini slump test and rheological testing. The addition of two chemical agents (sodium gluconate and a commercial hydration stabilizer sold under the trade name "Recover") as chemical admixtures was shown to increase the workable time of the geopolymer pastes, while additions of borax, naphthalene sulfonate, and sodium sulfate could not improve the workability. Optimum dosages to improve the workability for sodium gluconate and Recover additions were 0.35% and 1.50% by mass of the fly ash, respectively, when the paste was mixed using a mixer as prescribed in ASTM C305. However, additions of

sodium gluconate and Recover at the optimum dosages resulted in reductions in compressive strength of the geopolymer pastes compared to the pastes without chemical admixtures. Fumed silica was also added as a chemical admixture to NaOH solution with Ms = 1; fumed silica was added to obtain a molar ratio SiO_2/Na_2O of 1. The pastes prepared with fumed silica addition sustained large mini slump areas for over 60 minutes for all fly ashes. However, the fumed silica addition increased the compressive strengths for WP and BC fly ashes, but resulted in significant drops in the strengths for MR fly ash. Workability was impacted by the mixing process used to prepare the paste. High shear mixing at 1000 rpm extended workable times with similar initial mini slump areas of the pastes. This study showed that it is possible to control the workable times of alkali-activated high calcium, Class C fly ash, but this can come at a cost of reduced compressive strength.

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Chapter 1: Introduction and Background

1.1 Introduction

Geopolymers are aluminosilicate-based materials that can be synthesized by alkaline activation of various source materials such as metakaolin, blast furnace slag, and coal fly ash. This work focused on high-calcium fly ash geopolymers, which have low workability and rapid setting times compared to geopolymers synthesized from other sources of aluminosilicate material. The chemical composition and reactivity of fly ash are suitable to be used in new cementitious material development including geopolymer synthesis. Rapid stiffening behavior of high-calcium fly ash geopolymers limits the development and potential use of high-calcium fly ash as a source material for geopolymers. However, in some areas where lignite is used as a source of energy in power stations, high-calcium fly ash is obtained as the fine portion of coal combustion and it is discarded at landfill sites as a waste material if left over. Incorporation of a chemical admixture that improves the workability to the geopolymer system can enable the use of high-calcium fly ash in geopolymer synthesis.

The goal of the work presented in this thesis was to find a solution to prolong the workable time of a geopolymer paste without compromising strength development of the paste. Three sources of high-calcium fly ash were used in the study. Effects of chemical admixtures, mixing intensity, and fumed silica addition on properties of the geopolymer pastes were investigated. The chemical admixtures selected were reagent grade chemicals and commercial admixtures that have been used as retarders for portland cement concrete.

Workability of the geopolymer pastes was assessed by a mini slump test and shear rheometer.

1.2 History and development of geopolymers

Geopolymers are a new class of inorganic materials that can be synthesized from the reaction of a solid aluminosilicate with a concentrated aqueous alkali hydroxide or silicate solution. They were first studied in 1972 at the Cordi-Géopolymère private research laboratory in France and the first geopolymer cement, also known as Pyrament cement, was developed in 1986 at Lone Star Industries in the USA [1]. Geopolymers are also referred to in the literature as inorganic polymers, mineral polymers, alkali-bonded ceramics, and several other names. Geopolymers were initially used in fire-resistant applications as substitutes for thermosetting polymers, and they were further developed to be used in related applications such as coatings for fire protection, thermal protection of wooden structures, and heat-resistant adhesives. However, the primary uses for geopolymers have changed to being used as an alternative to portland cement in construction, transportation, and infrastructure since they can provide comparable performance to portland cement [2].

Geopolymer properties including the workability, setting behavior, and chemical and physical properties are influenced by various factors such as raw material, solution type, solution-to-solid ratio, and curing conditions [3]. Geopolymers can be formulated to possess specific properties and characteristics including fast or slow setting, high compressive strength, low shrinkage, fire resistance, and acid resistance.

1.3 Reaction mechanism for geopolymerization

Although the mechanism of setting and hardening during geopolymerization is not fully understood [4, 5], there are proposed models that try to explain the alkali activation of aluminosilicate materials. A general mechanism of geopolymerization is proposed by Glukhovsky [4, 6]. In this model, geopolymerization is divided into three main steps which are destruction-coagulation, coagulation-condensation, and condensation-crystallization.

In destruction-coagulation, an alkaline solution is combined with a reactive aluminosilicate powder, and the aluminosilicate material provides silicate and aluminate species, mostly in monomeric form, by alkaline hydrolysis. During alkaline hydrolysis, the covalent bonds between Si-O-Si, Al-O-Al, and Al-O-Si are broken by the action of the hydroxyl ions as they redistribute the electron density around the bonds, which makes the bonds more susceptible to break. At high pH, the dissolution of reactive aluminosilicate material is rapid, which creates a supersaturated aluminosilicate solution. Then, silicate, aluminate, and aluminosilicate start to form complexes in the concentrated solution [4, 6].

In the coagulation-condensation stage, isolated complexes accumulate, and large networks are formed by polycondensation from the aqueous phase. During polycondensation, the water consumed in alkali hydrolysis is released. Therefore, the water only acts as a reaction medium in geopolymerization to improve workability and it will stay within pores, not incorporated in the structure.

While the networks continue to rearrange and reorganize, the connectivity of the gel networks also increases during condensation-crystallization. Consequently, three-dimensional networks are formed, which is a common characteristic of geopolymers. This

stage regulates the microstructure and pore distribution of the geopolymeric materials, which affect their physical properties.

A highly simplified reaction mechanism for geopolymerization proposed by Duxson et al. [6] is shown in Figure 1.1. It should be noted that the model neglects the possibility of fine grinding and heat treatment of raw materials, which affect the dissolution of aluminosilicate materials.

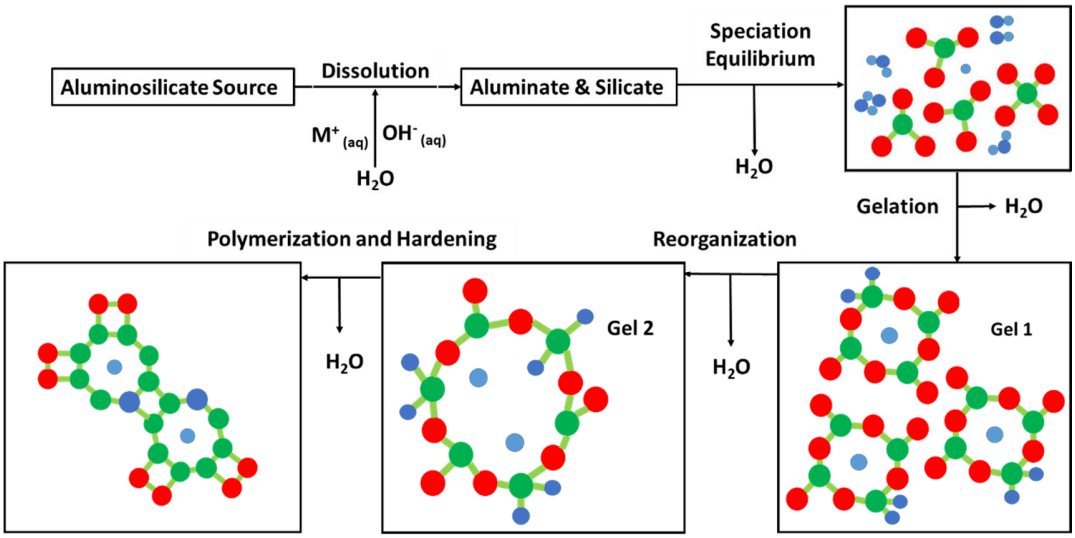

Figure 1.1: Simplified reaction mechanism for geopolymerization adapted from Duxson et al. [6]

The aluminosilicate source materials can be industrial by-products such as coal fly ash and blast furnace slag, or thermally activated natural materials such as kaolinite clay. They are categorized into two main groups based on the main reaction products: materials containing Ca-Si-Al, e.g. blast furnace slag, and materials containing Si-Al, e.g. metakaolin and Class F fly ash. Calcium silicate hydrate (C-S-H) is the main reaction product formed by alkali activation of blast furnace slag. For metakaolin and Class F fly ash, alkaline

aluminosilicate (N-A-S-H gel) with silica and alumina tetrahedra in the structure is the main reaction product. A structural model proposed for N-A-S-H is shown in Figure 1.2 [6].

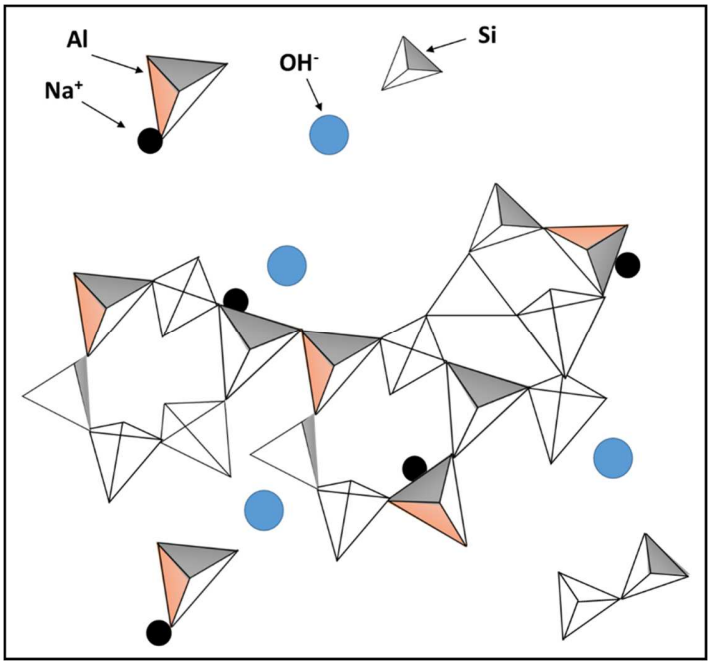

Figure 1.2: Structural model proposed for N-A-S-H adapted from Criado [6]

C-S-H composition and structure can be influenced by many factors, for example, temperature, pH, alkalis, and relative humidity [6]. These factors also affect the composition and structure of the alkaline aluminosilicate gel. The structural model proposed for the three-dimensional network of the alkaline aluminosilicate gel contains silica and alumina tetrahedra with alkali cations acting as charge balance elements when Si(IV) is replaced by Al(III). It also should be noted that geopolymers are in the same aluminosilicate family as zeolites, but they have an amorphous structure [7].

The final network from geopolymerization is mainly determined by the Si-to-Al ratio. Depending the relative amount of Si and Al, the repeating unit of geopolymers varies from sialate [-Si-O-Al-O-], sialate-siloxo [-Si-O-Al-O-Si-O-], to sialate-disiloxo [-Si-O-Al-O-Si-O-Si-O-], which correspond to Si-to-Al ratios of 1, 2, and 3, respectively [8]. Generally, the ratio is controlled in the range of 2 to 3.5 for materials used in transportation infrastructure, and the geopolymers exhibit improved compressive strengths when the Si-to-Al ratio is between 3.16 and 3.46. However, the compressive strengths drop as the ratio exceeds 3.85 [5].

1.4 Fly ashes as the aluminosilicate source for geopolymer synthesis

Aluminosilicate source materials for making geopolymers are calcined clays (composed mainly of metakaolin), ground granulated blast furnace slag (GGBFS), and coal fly ashes. These materials have been extensively used as supplementary cementitious materials (SCMs) in the cement industry. Calcined clays have been studied and used as a raw material for geopolymer synthesis. However, the plate-like shape of metakaolin particles usually resulted in high water demand and high porosity in the microstructure of geopolymer concrete [9]. In addition, metakaolin is not extensively used due to its high cost [3].

Fly ash is the most common source for geopolymer production. Due to the slow reactions of fly ash at ambient temperature, initial curing at a temperature between 40 and 95°C is generally required for the geopolymers to obtain high compressive strengths [10]. However, fine grinding of fly ash has been shown to improve the reactivity and has resulted in relatively higher compressive strengths of the geopolymer pastes for specimens were

cured at ambient temperature [10]. Depending on the calcium content, fly ashes can be categorized as high calcium, or Class C fly ash, and low calcium, or Class F fly ash. Low-calcium fly ash is obtained from burning bituminous coals, while burning of lignite and subbituminous coals gives high-calcium fly ash. High-calcium fly ash geopolymers have rapid setting times compared to geopolymer binders obtained from low-calcium fly ash or metakaolin, which limits the development and potential use of Class C fly ash as a source of aluminosilicate for geopolymers. Final setting has been shown to occur within 1-2 hours at room temperature and was attributed to the early formation of C-S-H [11]. Most works published on fly ash geopolymers are based on low-calcium fly ash.

Typical compositions of high-calcium fly ash are in between those of low-calcium fly ash and GGBFS. Since mixtures of low-calcium fly ash and GGBFS have been used in geopolymer production, high-calcium fly ash has potential to be used in future applications provided that the flowability of the geopolymer mix can be controlled [12].

1.5 Alkali activators for geopolymer synthesis

Common alkali activators used for synthesizing geopolymers are sodium hydroxide, potassium hydroxide, sodium silicate and potassium silicate. Dissolution of amorphous silica and alumina from fly ashes varies with the type and concentration of the alkali activators. The solubility of Al^{3+} and Si^{4+} ions in NaOH solution is higher than in KOH solution, which makes NaOH solution more suitable for the activation of fly ash. Use of a mixed activator of NaOH and sodium silicate improves the compressive strength of the geopolymer compared to when only NaOH solution was used, since the sodium silicate increases Si content in the reaction products [13].

Work by Görhan and Kürklü [13] showed that with a SiO_2/Al_2O_3 molar ratio of 3, the amount of dissolution changes with the NaOH concentration and the dissolution time. Strength gain of low-calcium fly ash geopolymer mortars was promoted by increasing curing temperature (65°C and 85°C) and curing time (2, 5 and 24 hours). The strength increase was attributed to enhanced reactions between silica and alumina in the alkali solution. However, strength gain of the specimens cured at elevated temperatures was not achieved when either too high or too low alkali concentration was used for geopolymer synthesis. A weak chemical reaction occurred in a too low alkali solution (3 M NaOH), and the coagulation of silica was expected to be the cause of the reduction in strength with a too high alkali solution (9 M NaOH). The highest mortar compressive strengths of 21.3 and 22 MPa were obtained from the fly ash activated by 6 M NaOH and cured at 65°C and 85°C for 24 hours, respectively [13].

In a study by Somna et al. [10], high-calcium fly ash geopolymers were activated by NaOH solution with concentrations of 4.5, 7.0, 9.5, 12.0, 14.0 and 16.5 M. The compressive strength of geopolymer pastes was improved with an increase in NaOH concentration from 4.5 to 14.0 M. The strength of geopolymer pastes decreased with 16.5 M NaOH solution since excess hydroxyl ion concentration caused precipitation of aluminosilicate products at very early stage [10]. 28-day compressive strengths of 20-23 MPa were obtained with 9.5 to 14.0 M NaOH solutions when the geopolymer pastes were cured at room temperature. The NaOH concentration also affected the dissolution of silica and alumina from the fly ash. From energy dispersive X-ray spectroscopy (EDS) analysis,

the Si/Al ratios were in the range of 1.14-1.54. Leaching of Al was promoted at higher NaOH concentrations resulting in reduced Si/Al ratio.

Hanjitsuwan et al. [14] showed that with increasing NaOH concentrations of 8, 10, 12, 15 and 18 M (sodium silicate to sodium hydroxide ratio of 0.67), the strength of high-calcium fly ash geopolymer pastes increased and the initial and final setting times were also prolonged from 30 and 125 minutes to 120 and 250 minutes, respectively. The improved workability of the pastes was associated with leaching of silica and alumina from the fly ash since the leaching of silica and alumina was better at high NaOH concentrations. As a consequence, the leaching of calcium was hindered, resulting in a limited amount of calcium in the solution. The setting of the paste was governed by the normal geopolymerization process. At low NaOH concentration, the leaching of calcium ions to the solution was not hindered. The calcium content was adequate for the precipitation, which caused the formation of C-S-H and calcium aluminate hydrate. The setting time of geopolymer pastes with low NaOH concentration solutions was correlated with the amount of calcium in the solution and therefore controlled by the formation of C-S-H and calcium aluminate hydrate. Higher dissolution of silica and alumina in high NaOH concentration solutions also contributed to increased formation of N-A-S-H and higher compressive strength of the high-calcium fly ash geopolymer pastes. In addition, a relatively dense matrix with less unreacted fly ash particles was also observed for the geopolymer pastes with high NaOH concentration solution with scanning electron microscopy [14].

Setting and hardening characteristics of geopolymers have been observed to change with the SiO_2 and Al_2O_3 contents of the geopolymer mixture. For conventional low-calcium

fly ash geopolymers, the setting time is reduced with an increase in Al_2O_3 content, while higher SiO_2 content leads to prolonged setting time and low-porosity microstructures [11]. For high-calcium fly ash geopolymers, increased SiO_2 or Al_2O_3 contents limit the workable time. C-S-H, C-A-S-H, and N-A-S-H are common phases found in high-calcium geopolymer systems. Formation of C-S-H or C-A-S-H in the early stages is responsible for the setting of high-calcium fly ash geopolymers, and it is mainly controlled by SiO_2/Al_2O_3 ratio rather than calcium content in solution [11]. Strength development of the geopolymer is associated with the formation of N-A-S-H. An optimum SiO_2/Al_2O_3 ratio in terms of strength development and setting behavior has shown to be in the range of 3.20-3.70 [11].

For mixed alkali activators with SiO_2/Na_2O ratios of 1.0, 1.5 and 2.0, the content of the mixed activator was varied by Guo et al. [12] to obtain the mass proportion of Na_2O to fly ash of 6-15%. The compressive strength of high-calcium fly ash geopolymers increased with higher alkali content until the mass proportion of Na_2O to fly ash reached 10%. The strength gain was not significant when the activator content was further increased. The highest compressive strengths were obtained with a molar ratio SiO_2/Na_2O of 1.5 for all activator contents [12].

Since typical geopolymer composition is denoted as $nM_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$, where M is an alkali metal usually obtained from alkali activators, microstructures and properties of alkali-activated fly ash geopolymer depend on the SiO_2/Al_2O_3 and Al_2O_3/Na_2O ratios. When mixed with 6, 9 and 12 M NaOH solution, Ryu et al. [15] showed that the compressive strength of low-calcium fly ash geopolymer mortars increased with higher NaOH concentration, and the effect was significant at the early ages. Compressive

strengths at 56 days of greater than 45 MPa were obtained with 9 and 12 M solutions when the samples were cured at 60°C for 24 hours. For the specimens prepared with different ratios of 9 M NaOH: sodium silicate, the compressive strength decreased with higher SiO_2/Na_2O (6.5-10.0) and Al_2O_3/Na_2O (1.65-2.40) ratios. In particular, the strengths were significantly reduced when SiO_2/Na_2O and Al_2O_3/Na_2O were greater than 8.01 and 1.94, respectively [15].

The concentration of NaOH and the ratio of sodium silicate to NaOH has been shown to affect the workability of geopolymer mortar, as demonstrated by Chindaprasert et al. [16]. The flow of high-calcium geopolymer mortar decreased with an increase in NaOH concentration (10 M, 15 M and 20 M) and in sodium silicate to NaOH ratio (0.67, 1.00 and 1.50). To obtain a high strength geopolymer mortar, the optimum range of sodium silicate to NaOH was 0.67 to 1.00, and the NaOH concentration in this range was found to have small effect on the strength of mortar. The workability of the geopolymer mortar could be improved by adding extra water or superplasticizer. However, addition of superplasticizer caused a larger reduction in the strength of geopolymer than the mortar with extra water. It was suggested that use of superplasticizer was not required when fly ash based geopolymers were made with a mixture of NaOH and sodium silicate [16].

Use of a multi-compound activator $Na_2SiO_3/NaOH = 2.5$ with a SiO_2/Na_2O ratio of 2.0 by Nematollahi and Sanjayan [17] resulted in improved flowability and higher compressive strength of a low-calcium fly ash geopolymer paste compared to a geopolymer paste activated by NaOH solution. Nevertheless, the viscosity of the paste activated by multi-compound activator was significantly higher [17].

1.6 Effect of chemical admixtures on workability of geopolymer

For portland cement concrete, chemical admixtures are introduced during concrete mixing to modify fresh or hardened properties of the concrete. The most common types of chemical admixtures used in portland cement concrete are water reducers, retarders, accelerators, plasticizers and air entrainers. Since low workability or rapid setting behavior is the main concern for high-calcium fly ash geopolymers, incorporation of chemical admixtures may improve the workability of the geopolymers.

Superplasticizers (SPs), or high range water reducing admixtures (HRWRAs), are chemical admixtures added to portland cement concrete to get a well-dispersed particle suspension. The purpose of using superplasticizers with respect to workability considerations is to reduce the water content while maintaining a constant workability or to increase flowability with the same water content. Common types of superplasticizers include lignosulfonate, naphthalene- and melamine-based, and modified polycarboxylates.

The compressive strength and workability of low-calcium fly ash geopolymer pastes has been shown to vary with different types of alkali solutions and superplasticizers by Nematollahi and Sanjayan [17]. In that study, a naphthalene-based superplasticizer significantly improved the slump of geopolymer paste (136% increase) activated by 8 M NaOH solution (SiO_2/Na_2O ratio of 2.0) without causing any drop in the compressive strength compared to the paste without any superplasticizer. A naphthalene-based superplasticizer was used, since naphthalene-based superplasticizers are the only type of superplasticizer that is chemically stable in that high alkali solution [17]. However, all types of superplasticizers with the dosage of 1% by mass of fly ash resulted in decreases

in compressive strength of the geopolymer pastes activated by a multi-compound activator with Na_2SiO_3/NaOH = 2.5. The strength reductions were 15-29% for polycarboxylates and 42-51% for naphthalene- and melamine-based superplasticizers. In addition, the increases in relative slump were 39-45% for polycarboxylates and only 6-8% for naphthalene-based superplasticizer. A decrease in relative slump of 3% was obtained when the melamine-based superplasticizer was used. The instability of the superplasticizers in the multi-compound activator was expected to be the cause of strength reductions [17].

Retarders are chemical admixtures used in concrete to prolong workable time. The prolonged workable time generally involves reduction in the solubility of the hydrating components in the system. Effects of selected chemical admixtures including calcium chloride ($CaCl_2$), calcium sulfate ($CaSO_4$), sodium sulfate (Na_2SO_4), and sucrose on the compressive strength of high-calcium fly ash geopolymer and the setting time have been investigated by Rattanasak et al. [18]. The high-calcium fly ash geopolymer pastes were activated by a multi-compound activator with Na_2SiO_3/NaOH = 1.5 and solid/total mixture ratio of 0.6. For $CaCl_2$, additions of 1 wt% and 2 wt% decreased both initial and final setting times of the fly ash geopolymer compared to the geopolymer paste without chemical admixture. The cause of reductions in the setting times was attributed to to the flocculation of C-S-H that formed around the fly ash particles. The changes in the initial and final setting times were negligible when $CaSO_4$ was added to the pastes. Addition of Na_2SO_4 at dosages of 1 wt% and 2 wt% considerably delayed the initial setting time, while maintaining the final setting time, since Na_2SO_4 provided sulfate to the solution, resulting in the formation of ettringite around the fly ash particles which could impede the leaching of silica and

alumina from the fly ash particles. Addition of sucrose at dosages of 1 wt% and 2 wt% did not affect the initial setting time, whereas the final setting time was significantly delayed. Addition of 1 wt% addition of $CaCl_2$, $CaSO_4$, Na_2SO_4 and sucrose increased the compressive strength of the geopolymer mortars by 9-25%. However, 2 wt% addition of $NaSO_4$ resulted in smaller increases in the strength (3-6%) or strength reduction. In the microstructure of the geopolymer pastes, C-S-H and aluminosilicate gel were formed on the surface of the fly ash particles for the control paste with no chemical admixture and the paste with $CaCl_2$. Ettringite was observed for the pastes with $CaSO_4$ and Na_2SO_4. For the paste with sucrose, small particle agglomerates were detected on the surface of the fly ash particles [18].

Chapter 2: Materials and Methods

2.1 Materials

The materials used in the study including fly ashes, portland cement, alkali activating solutions, and chemical admixtures are described in this section.

2.1.1 Fly ashes

Three sources of high calcium fly ash from different plants in the United States were used. The chemical compositions of the fly ashes, analyzed by x-ray florescence, are shown in Table 2.1.

Table 2.1: Chemical composition of fly ash (mass %)

Oxide	WP	BC	MR
Al_2O_3	17.44	17.51	19.59
SiO_2	32.55	35.79	37.00
CaO	28.95	26.89	23.88
Fe_2O_3	5.48	5.99	6.32
K_2O	0.46	0.56	0.54
MgO	6.45	6.25	4.76
Na_2O	1.86	1.96	1.73
SO_3	2.98	1.99	2.01
TiO_2	1.32	1.15	1.42
P_2O_5	0.89	0.81	1.20
Na_2O_{eq}	2.16	2.33	2.09

2.1.2 Portland cement

Portland cement used in the study was portland cement Type I/II from Alamo Cement (July 2013).

2.1.3 Alkali activating solutions

Sodium hydroxide solutions were used for all specimens in this study. The concentration of NaOH solutions was 4 M, and the solutions were prepared by diluting an extra pure 50 wt% NaOH solution from ACROS Organics with ultrapure water from a Nanopure water purification systems. The NaOH solutions were allowed to rest at room temperature for at least 24 hours before they were used. For some solutions, fumed silica was added to NaOH solution to obtain the molar ratio SiO_2/Na_2O of 1 and the solutions were rested at room temperature at least 24 hours before they were used. The fumed silica was Aerosil 200 from Evonik industries.

2.1.4 Chemical admixtures

Chemical admixtures used in this study were tested for the potential use to improve workability of the alkali-activated fly ash geopolymers.

Sodium gluconate and sodium tetraborate decahydrate (borax) were reagent grade chemicals from Sigma-Aldrich, and sodium sulfate anhydrous was a reagent grade chemical from Fisher Chemical.

Sikament N is a high range water reducing admixture that contains sodium naphthalene sulfonate as the main ingredient. It has specific gravity of approximately 1.21. It meets the requirements of ASTM C494 as Type A and F admixture. For general concrete applications, dosage rates of 6 to 20 oz/100 lbs (390-1000 mL/100 kg) of cementitious materials are recommended by the manufacturer of Sikament N.

Recover is an aqueous solution of hydroxycarboxylic acid salts and compound carbohydrates which has sodium gluconate, sucrose, and water as the main ingredients. It

has specific gravity of approximately 1.15. It is a hydration stabilizer from W.R. Grace and complies with ASTM C494 as a Type D retarder. For traditional applications, dosage rates of 2 to 6 oz/100 lbs (130 to 390 mL/100 kg) of cement are used.

2.2 Methods

The methods for mixing of the fly ash and the alkali solution, compressive strength test, and mini slump loss test are described in this section.

2.2.1 Mixing procedures

The alkali-activated fly ash pastes were prepared using a planetary mixer (Hobart N50) or an overhead high shear mixer (SCILOGEX OS40-S). A mass ratio of NaOH solution to fly ash (solution-to-powder ratio) of 0.45 was used for all specimens. When using the planetary mixer, the mixing procedures followed the mixing procedures for pastes as described in ASTM C 305 [19]. For the planetary mixer, the first speed revolves the paddle at a rate of 140 $\pm$ 5 r/min, with a planetary motion of approximately 62 r/min. The second speed revolves the paddle at a rate of 285 $\pm$ 10 r/min, with a planetary motion of approximately 125 r/min. The mixing procedures for the overhead high shear mixer were as follows:

1) Added the fly ash to the NaOH solution and rested for 30 s.
2) Started the mixer and mixed at 350 $\pm$ 10 rpm for 60 s.
3) Stopped the mixer for 30 s and scraped the paste collected on sides of the container.
4) Started the mixer and mixed at 1000 $\pm$ 10 rpm for 60 s.

For the pastes containing a chemical admixture, the admixture was added to the NaOH solution and stirred until completely dissolved in the solution before adding fly ash. For delayed addition of a chemical admixture, the admixture was added before mixing at 1000 rpm for high shear mixing.

2.2.2 Compressive strength testing

After mixing, the fresh paste was poured in 5.08-cm diameter and 10.16-cm height plastic cylinder molds with lids. The cast specimens were left at the room temperature for 1 hour and cured at 38°C and 95% humidity for 24 hours. They were demolded and cured at 23°C until the time of testing. During the compressive strength test, neoprene pads were used to assure load uniformity and the loading rate was controlled within 391-587 N/sec (88-132 lbf/sec). The compressive strength test was performed at the age of 7 and 28 days and the compressive strength values were the average of three specimens.

2.2.3 Mini slump loss testing

Workability of the fresh alkali-activated fly ash pastes was evaluated by mini slump test. The mini slump test followed the ASTM draft test method for measurement of cement paste consistency using a stainless steel mini slump cone [20]. The mini slump cone has dimensions of 40-mm diameter on the bottom, 20-mm diameter on the top, and a height of 60 mm. The paste was poured into the cone in a single pour and then it was tamped 15 times using spatula. Excess paste from the top was scraped off, and the cone was lifted gently in vertical direction. For each measurement, two perpendicular diameters of the patty were measured and the mini slump area was calculated from the average value of the diameters. The measurements were performed at 5, 10, 20, 30, 45, and 60 minutes. During

the test, the paste was always kept in a sealed container between measurement periods. The test was stopped when the mini slump area was less than 1500 mm^2.

2.2.4 Workability evaluation

After the geopolymer pastes were prepared using a high shear mixer as described in the mixing procedure section, the samples were transferred to mini slump cone and rheometer for testing and the tests were performed at 5, 20, 40, and 60 minutes. Rheological parameters of geopolymer pastes were determined by using Anton Paar MCR 301 rheometer equipped with a vane ST22-4V-40 with a diameter of 21.9 mm and a height of 40.3 mm. After the sample was loaded in the rheometer's cup, it was pre-sheared at 0.2 s^{-1} for 60 seconds to remove air voids that could be present in the sample. An initial pre-shear at 50 s^{-1} was used to ensure that all pastes were in the same reference state [21, 22]. The entire rheological testing protocol is outlined in Table 2.2.

Table 2.2: Testing protocol for rheology test

Test segment	**Function**	**Time (sec)**
1	Pre-shear at 0.2 s^{-1}	60
2	Rest	5
3	Pre-shear at 50 s^{-1}	30
4	Rest	10
5	Constant shear rate at 10 s^{-1}	30
6	Constant shear rate at 20 s^{-1}	30
7	Constant shear rate at 30 s^{-1}	30
8	Constant shear rate at 40 s^{-1}	30
9	Constant shear rate at 50 s^{-1}	30
10	Constant shear rate at 40 s^{-1}	30
11	Constant shear rate at 30 s^{-1}	30
12	Constant shear rate at 20 s^{-1}	30
13	Constant shear rate at 10 s^{-1}	30

2.2.5 Experimental matrix

The experimental matrix of the tests is summarized in Table 2.3.

Table 2.3: Experimental matrix

Test	**Measured parameters**	**Properties of the paste**
Mini slump loss	Diameter of the paste's spread	Workable time
Compressive strength	Maximum load	Compressive strength at 7 and 28 days
Rheometer	Shear stresses at different shear rates	Yield stress and viscosity

Chapter 3: Results and Discussion

Fly ash geopolymer pastes and portland cement pastes used in the study were prepared using the planetary mixer except for paste specimens in Sections 3.5, 3.10, and 3.12 which were prepared using a high shear mixer. The solution-to-powder ratio of geopolymer pastes and water-to-cement ratio of portland cement paste were maintained at 0.45, and the concentration of NaOH solutions was 4M for all specimens. Three sources of high calcium fly ash were used in this study: WP, BC, and MR.

3.1 Effect of sodium gluconate dosage on mini slump loss of geopolymer pastes

Sodium gluconate was used at dosages of 0.10%, 0.25%, 0.35%, and 0.50% by mass of the fly ashes to examine the effect that sodium gluconate dosage had on the slump retention behavior of the geopolymer pastes. Without chemical admixtures, the mini slump areas of all fly ash pastes were less than 1500 mm^2 since the first measurement at 5 minutes, as shown in Figure 3.1. The ASTM draft standard for mini slump [20] sets 1500 mm^2 as the workable limit for cement pastes, so this value was chosen as the workable limit for the geopolymer pastes. Figures 3.2-3.5 present the mini slump areas data for the pastes containing sodium gluconate. At 0.10% sodium gluconate, the workable time was prolonged to 10 minutes for WP and MR fly ashes, but the mini slump area at 5 minutes was still lower than the workable limit for BC fly ash. At 0.25% sodium gluconate, the workable times were 30 minutes for WP fly ash and 20 minutes for BC and MR fly ashes with initial mini slump areas of 9300-13400 mm^2. The initial slump areas were increased

to 12100-14900 mm^2 for the pastes with 0.35% sodium gluconate. In addition, the workable times were improved to 45 minutes for WP and MR fly ashes and 30 minutes for BC fly ash. By increasing the dosage of sodium gluconate to 0.50%, the mini slump areas at 60 minutes were greater than 1500 mm^2 for all fly ashes. However, the initial slump areas of BC and MR fly ashes decreased to 9400-10700 mm^2, and the initial slump areas of WP remained at approximately 14400 mm^2, as shown in Figures 3.6-3.8. At the dosage of 0.50%, the rates of slump loss for different sources of fly ash were varied where the slump loss rate of the WP fly ash was relatively high compared to the others. From the dosages of sodium gluconate tested, the optimum dosage to maximize the initial slump was chosen as 0.35% by mass of the fly ash since this kept pastes workable for at least 30 minutes.

At the same sodium gluconate dosage and time of measurement, the mini slump area also varied with source of the fly ash, and the slump areas were usually ranked in this order from lowest to highest areas: BC, WP, and MR. This could indicate different reactivities of the fly ashes, but there is no distinct variation in the chemical compositions for all fly ashes as shown in Table 2.1.

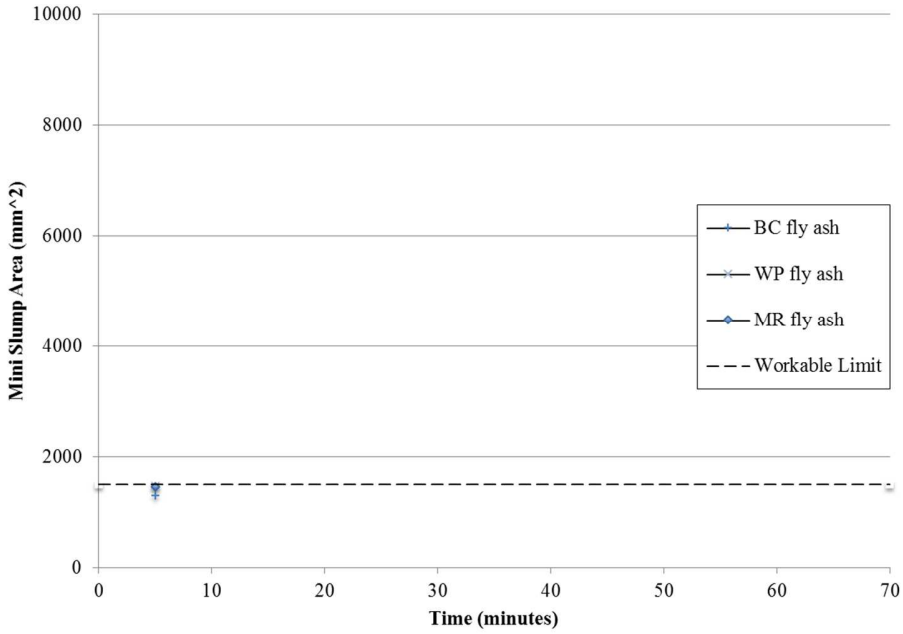

Figure 3.1: Mini slump area of geopolymer pastes without chemical admixtures

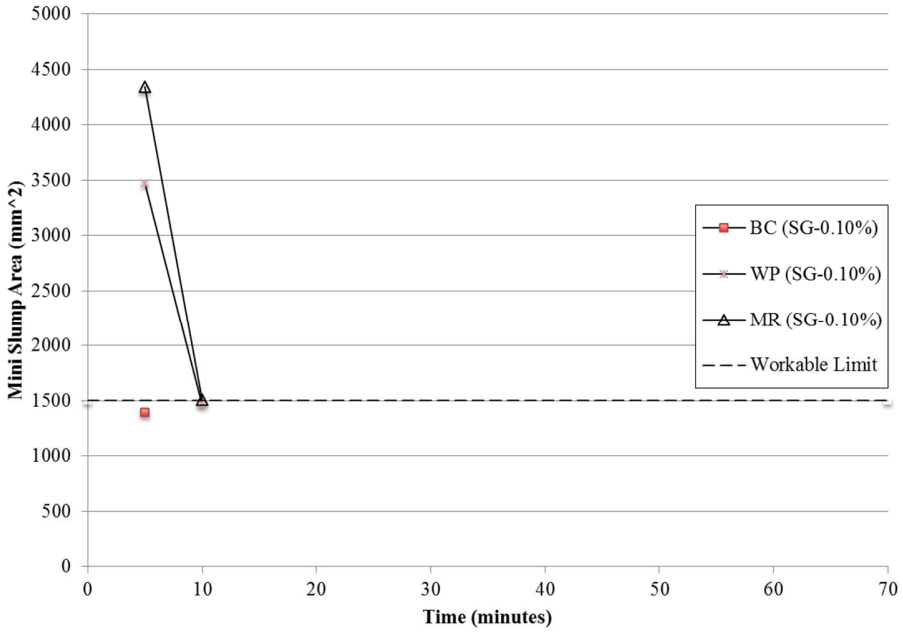

Figure 3.2: Mini slump area of geopolymer pastes with 0.10% sodium gluconate

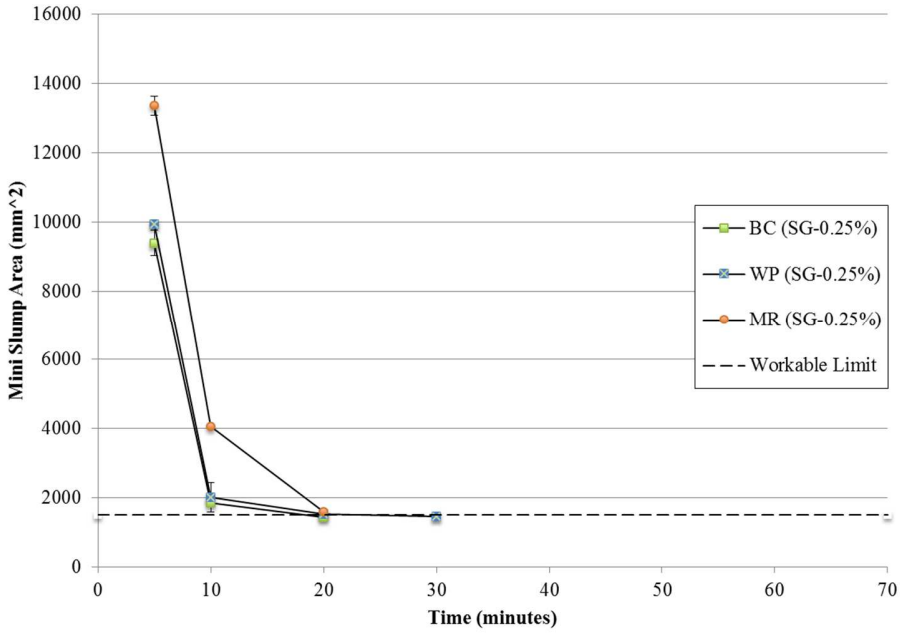

Figure 3.3: Mini slump area of geopolymer pastes with 0.25% sodium gluconate

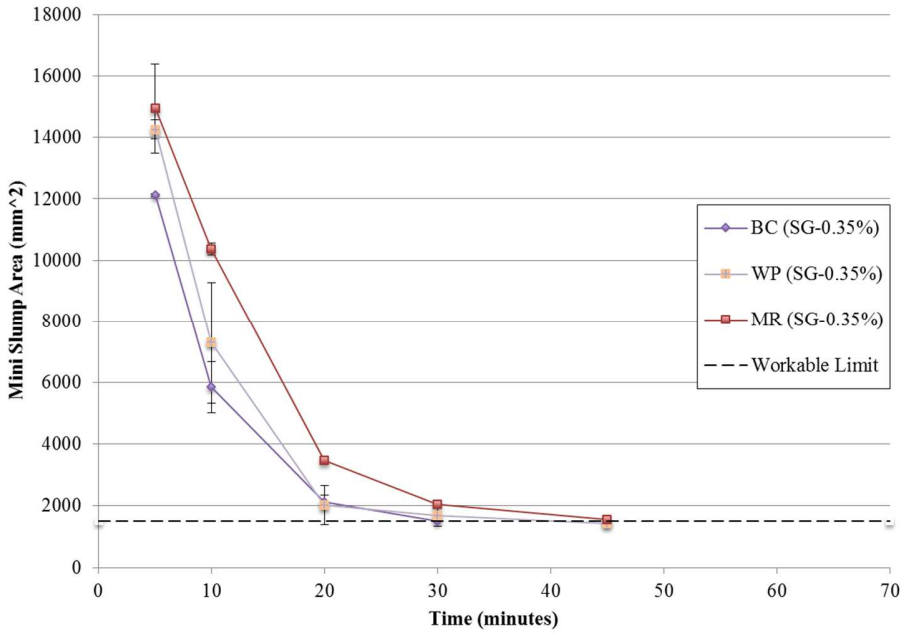

Figure 3.4: Mini slump area of geopolymer pastes with 0.35% sodium gluconate

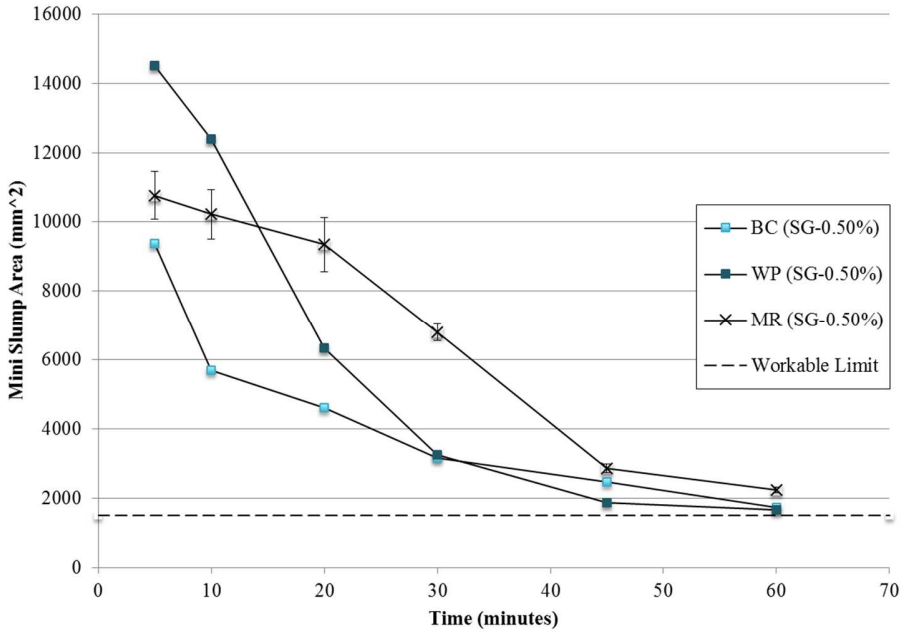

Figure 3.5: Mini slump area of geopolymer pastes with 0.50% sodium gluconate

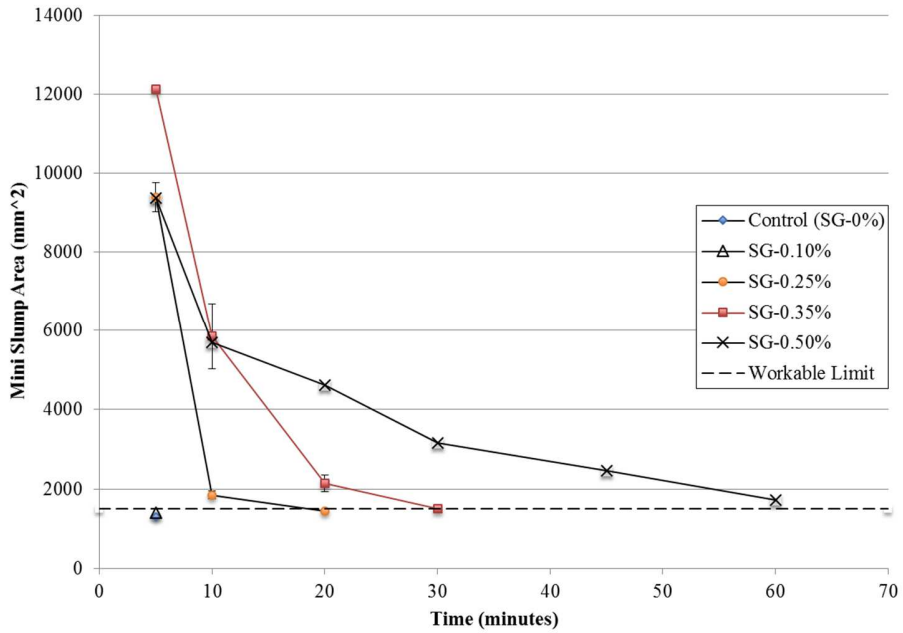

Figure 3.6: Mini slump area of BC fly ash geopolymer pastes with sodium gluconate

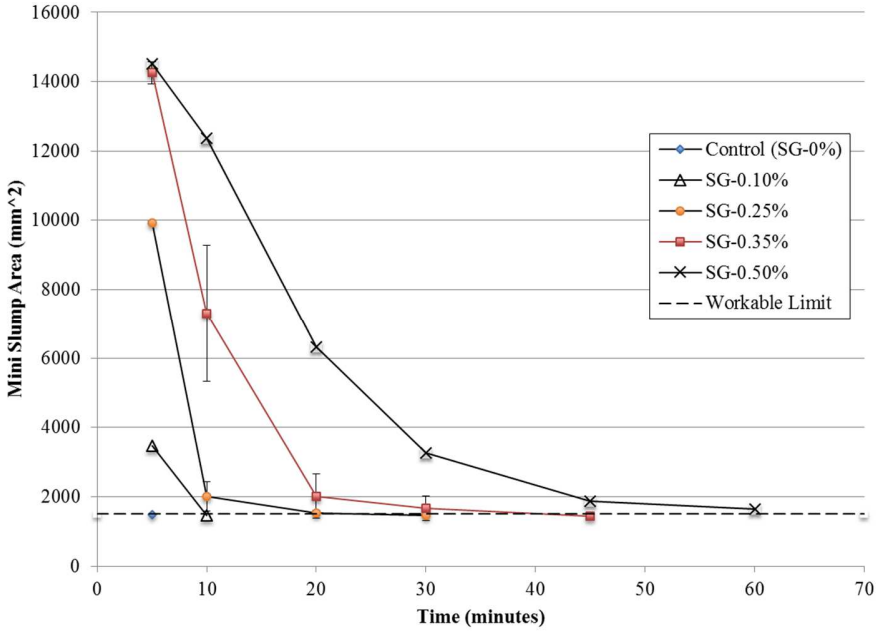

Figure 3.7: Mini slump area of WP fly ash geopolymer pastes with sodium gluconate

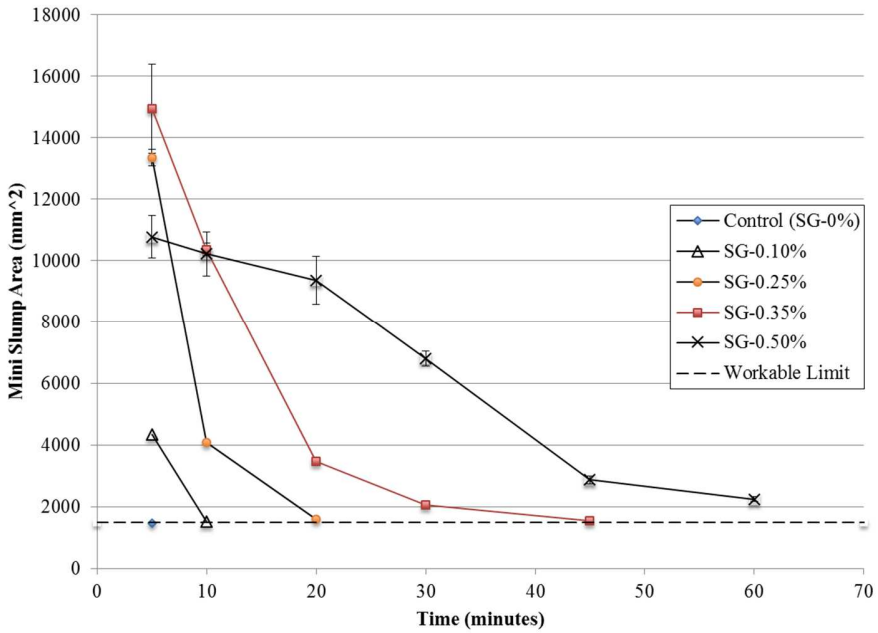

Figure 3.8: Mini slump area of MR fly ash geopolymer pastes with sodium gluconate

3.2 Effect of Recover dosage on mini slump loss of geopolymer pastes

For this study, Recover was used at the dosage of 1.00%, 1.25%, 1.50%, and 2.00% by mass of the fly ashes. Mini slump areas of the geopolymer pastes with different dosages of Recover are shown in Figures 3.9-3.12. At 1.00% Recover, the pastes maintained workable slump for 20 minutes for all fly ashes with initial slump areas of 4800-9800 mm^2. At 1.25% Recover, the workable times were 30 minutes for WP and MR fly ashes and 20 minutes for BC fly ash with initial slump areas of 6000-13600 mm^2. The workable times of the pastes with 1.50% Recover increased to 45 minutes for WP and MR fly ashes and 30 minutes for BC fly ash with initial slump areas of 6000-13600 mm^2. For 2.00% Recover addition, the mini slump areas at 60 minutes were still greater than 1500 mm^2 for all fly ashes and the initial slump areas were as high as 12500-18700 mm^2. The rates of slump loss for all fly ashes were high at the first 20 minutes and leveled off after that. Similarly to the sodium gluconate, it was decided that the optimal dosage should be that which allowed a workable time of at least 30 minutes, which was a dosage of 1.50% Recover.

For different sources of the fly ash with the same dosage of Recover, the slump areas of MR fly ash geopolymer pastes were greatest, followed by those of WP and BC fly ashes, respectively.

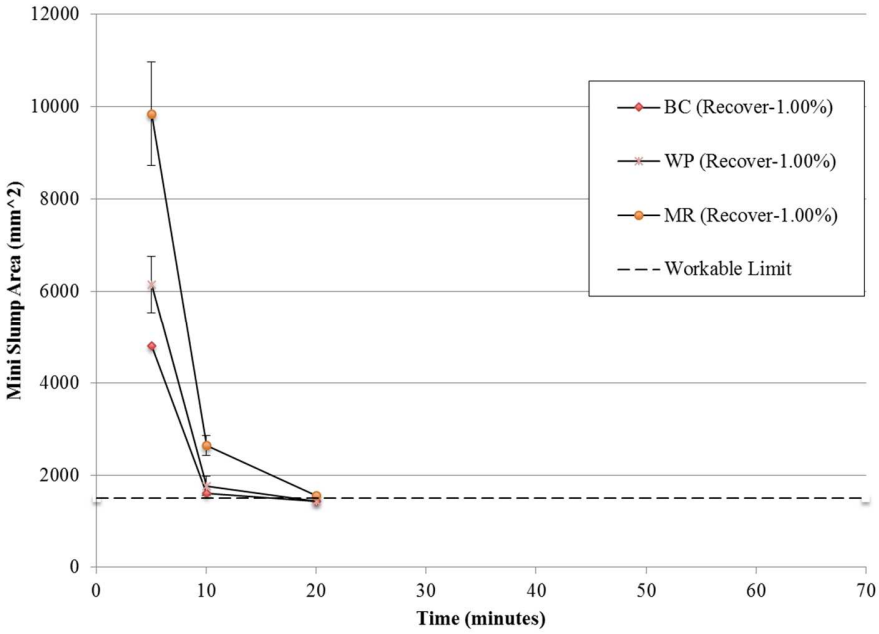

Figure 3.9: Mini slump area of geopolymer pastes with 1.00% Recover

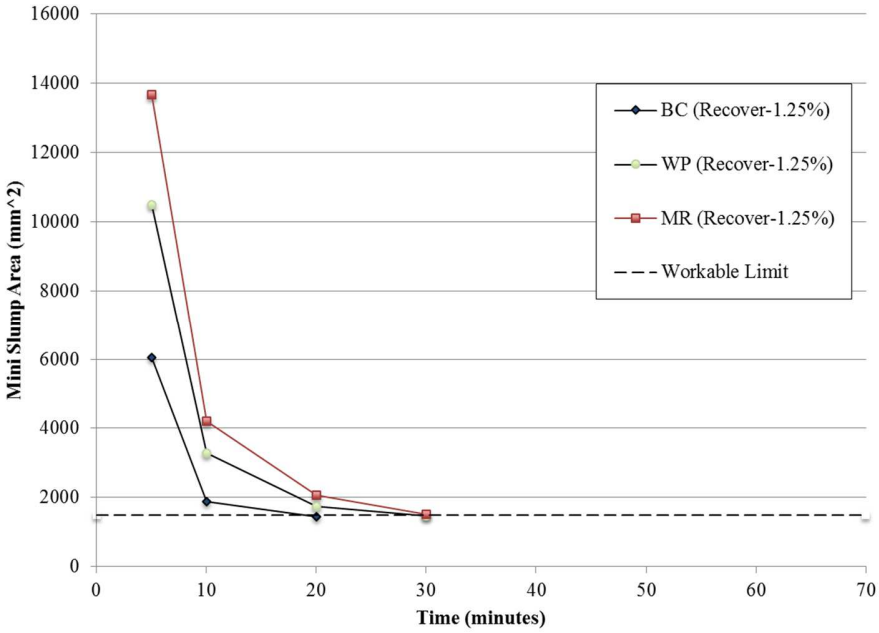

Figure 3.10: Mini slump area of geopolymer pastes with 1.25% Recover

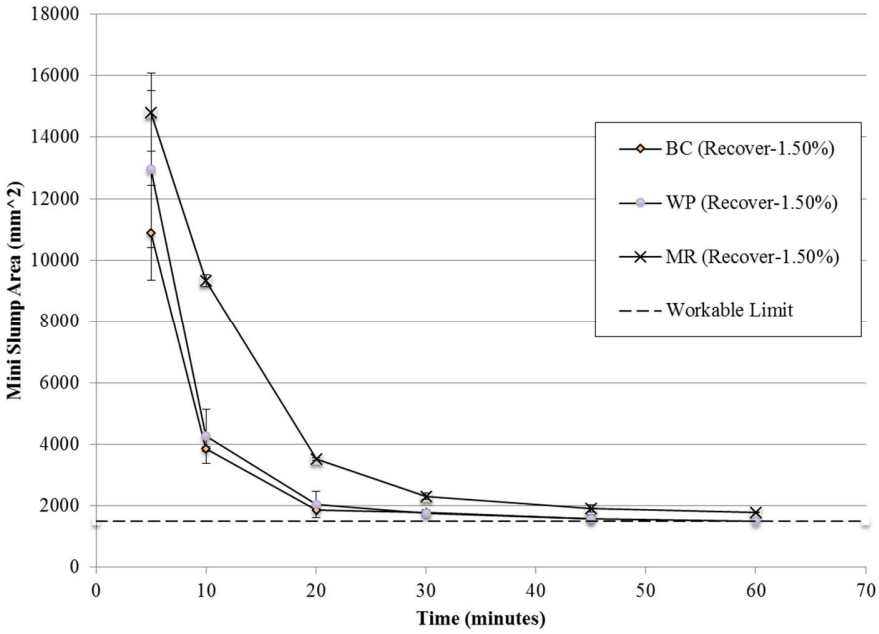

Figure 3.11: Mini slump area of geopolymer pastes with 1.50% Recover

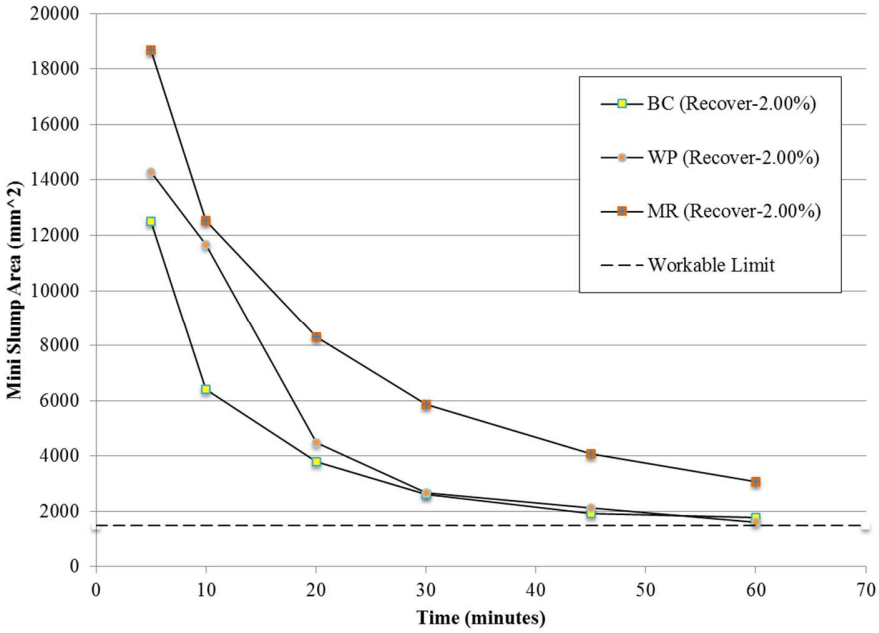

Figure 3.12: Mini slump area of geopolymer pastes with 2.00% Recover

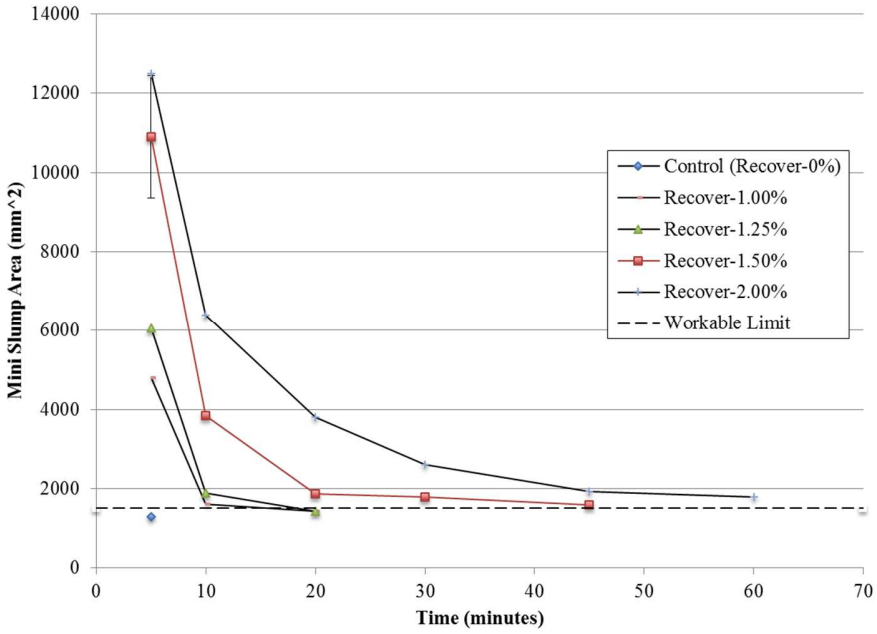

Figure 3.13: Mini slump area of BC fly ash geopolymer pastes with Recover

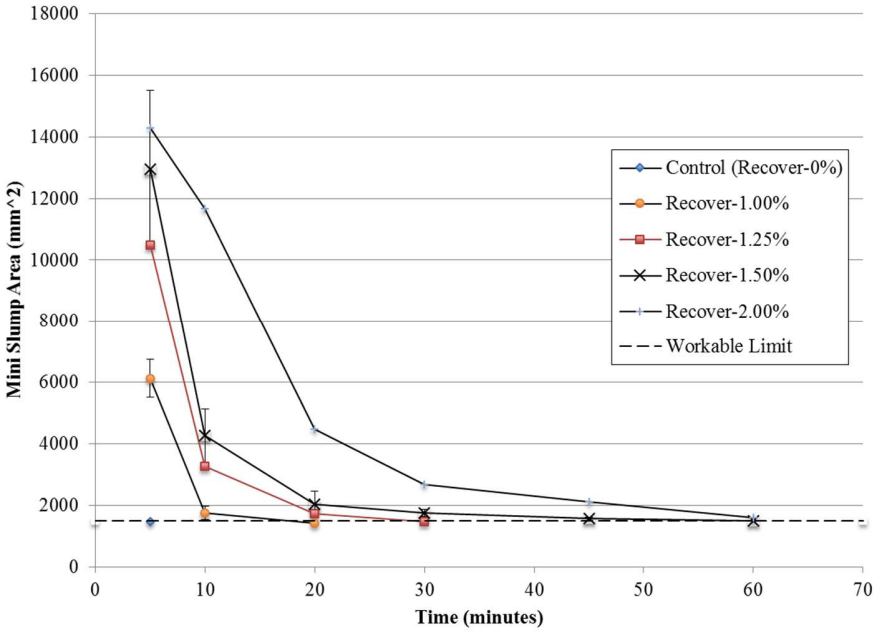

Figure 3.14: Mini slump area of WP fly ash geopolymer pastes with Recover

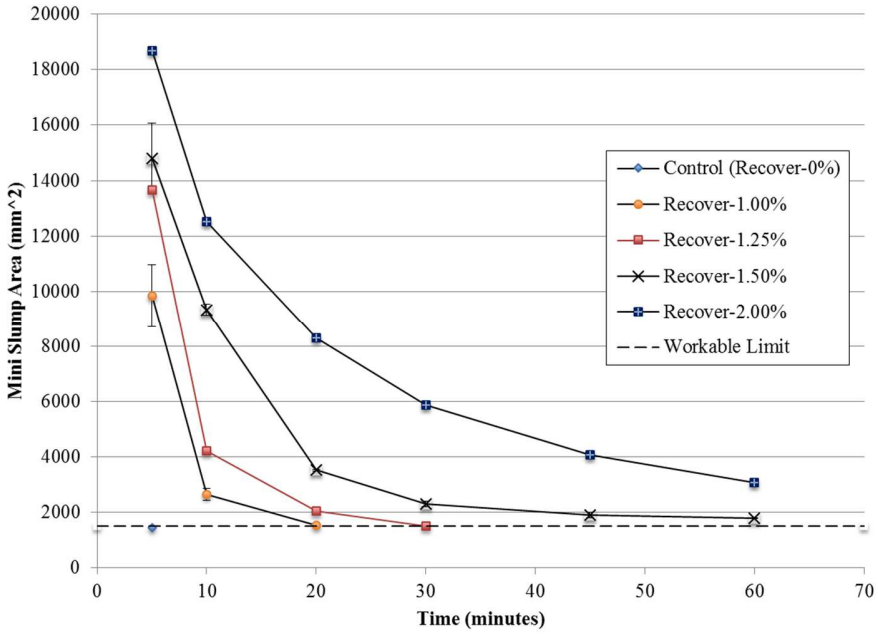

Figure 3.15: Mini slump area of MR fly ash geopolymer pastes with Recover

3.3 Effect of other chemical admixtures on mini slump loss of geopolymer pastes

Other chemical admixtures including borax (sodium tetraborate decahydrate), Sikament N (naphthalene sulfonate), and sodium sulfate were added to the geopolymer pastes to extend the workable time. However, none of these admixtures increased the mini slump area for the following dosages that were tested: borax (0.5%, 2%, 4%, 6%, and 10%), Sikament N (1%, 5%, and 10%), and sodium sulfate (1% and 5%) and the initial slump areas at 5 minutes were less than 1500 mm^2. In addition, borax and Sikament N at higher dosages appeared to increase the cohesiveness and stickiness of the geopolymer pastes.

3.4 Effect of chemical admixtures on mini slump loss of portland cement paste

Sodium gluconate and Recover were also tested with portland cement paste for the ability to improve slump flow and the results are shown in Figures 3.16-3.17. Unlike

geopolymer pastes, portland cement paste without chemical admixtures retained workable slump at 60 minutes, but the initial slump area was only about 4400 mm^2. With sodium gluconate, the initial slump areas were as high as 10400-11500 mm^2 for the pastes containing 0.20% and 0.30% sodium gluconate. The slump areas of the pastes with 0.20% and 0.30% sodium gluconate at 10 and 20 minutes were greater than the initial slump area, however, these pastes experienced significant bleeding at 10 and 20 minutes, as shown in Figure 3.18. It should be noted that the mini slump areas for the pastes with bleeding were calculated from the outer lengths of the pastes, not the largest diameters of the circular spread of the pastes.

For portland cement pastes with Recover, the mini slump areas of the pastes at the same time of measurement increased with increasing Recover addition (0.50%, 0.75%, and 1.00%). Similar to portland cement pastes with 0.20% and 0.30% sodium gluconate, the pastes with Recover also had the problem of stability of the mixture. The mixtures with 0.75% and 1.00% Recover had bleeding at 20 and 30 minutes, but the problem was not as severe as in the pastes with 0.20% and 0.30% sodium gluconate.

For portland cement pastes, the optimum dosages of sodium gluconate and Recover were considered to be 0.20% and 0.75%, respectively, since these dosages resulted in increased initial slump areas and only slight bleeding. The optimum dosage of Recover is within the range of the manufacturer’s recommended use.

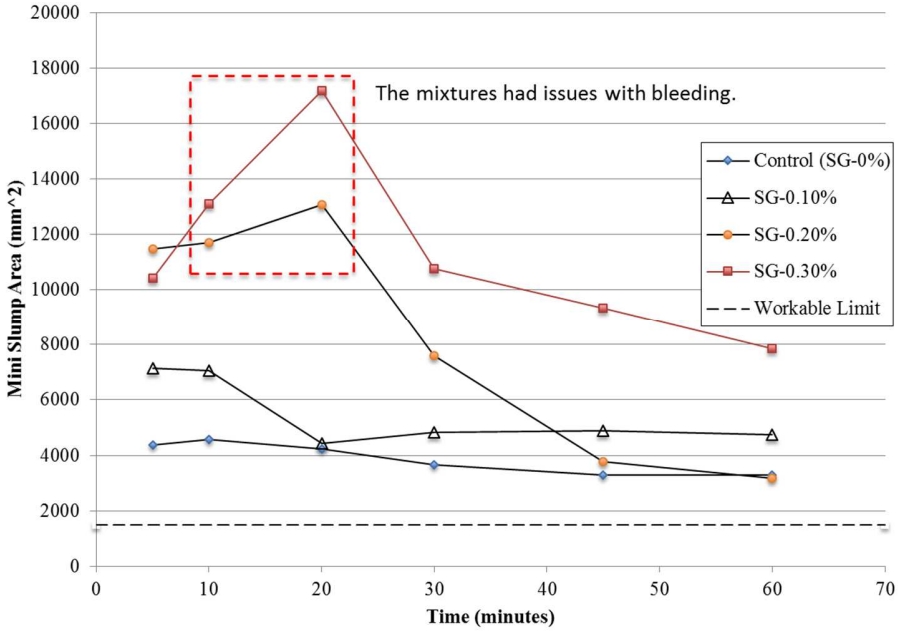

Figure 3.16: Mini slump area of portland cement pastes with sodium gluconate

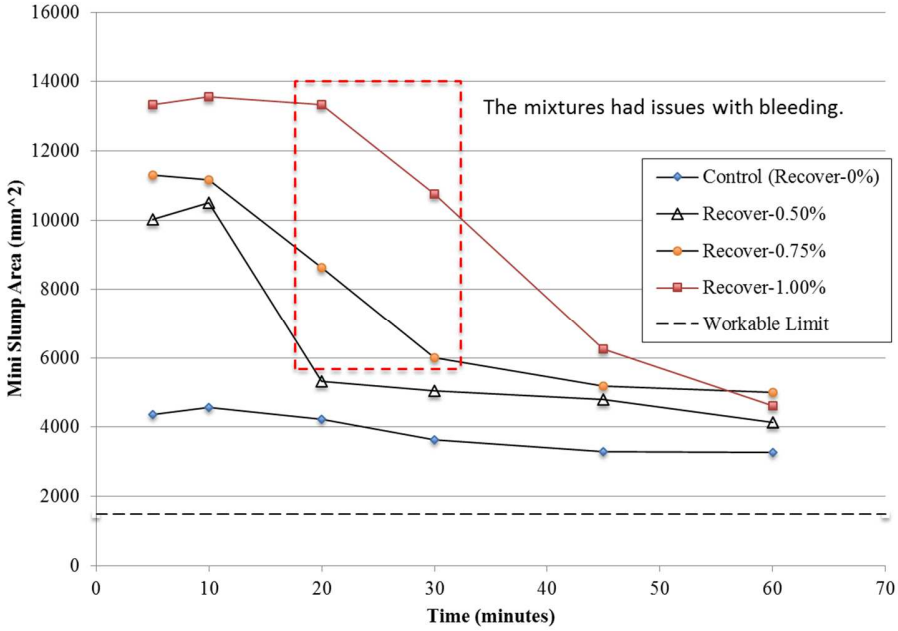

Figure 3.17: Mini slump area of portland cement pastes with Recover

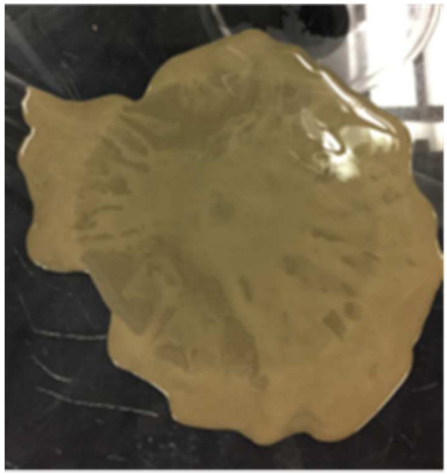

Figure 3.18: Mini slump flow of portland cement pastes with 0.30% sodium gluconate at 20 minutes

3.5 Effect of mixing intensity on mini slump loss of geopolymer pastes

In this section, BC and MR fly ashes were used to study for the effect of mixing intensity on mini slump flow of geopolymer pastes; the results are shown in Figures 3.19-3.27. The mixing procedures for high shear mixing are described in section 2.2.1. For the BC fly ash (Figure 3.19-3.21), the initial slump flows of the control paste, the paste with 0.35% sodium gluconate, and the paste with 1.50% Recover were not affected by the increase in mixing intensity. However, high shear mixing increased the slump flows at other measurement times and extended the workable times from 30 minutes for 0.35% sodium gluconate and 45 minutes for 1.50% Recover to more than 60 minutes.

For MR fly ash with sodium gluconate (0.25%, 0.35%, and 0.50%), high shear mixing also did not change the initial slump areas of the geopolymer pastes, but it improved the slump flows at other measurement times as shown in Figures 3.22-3.24. For 0.35% sodium gluconate, delayed addition of the admixture was also tested and sodium gluconate

was added just before mixing at 1000 rpm for this test, which is a 1.5 minute delay compared to the normal mixing procedure. The delayed addition of sodium gluconate also did not affect the initial slump area, but considerably improved the slump flow at other measurement times.

For MR fly ash with Recover (1.00%, 1.50%, and 2.00%), high shear mixing increased the initial slump area for 1.00% Recover, but decreased the initial slump areas for 1.50% and 2.00% Recover. However, the mini slump areas at other measurement times increased for all dosages.

One possible explanation for the effect of high shear mixing on slump flow of the geopolymer pastes is that microstructure of the geopolymer pastes was partly broken down by shear [23], resulting in improved flow.

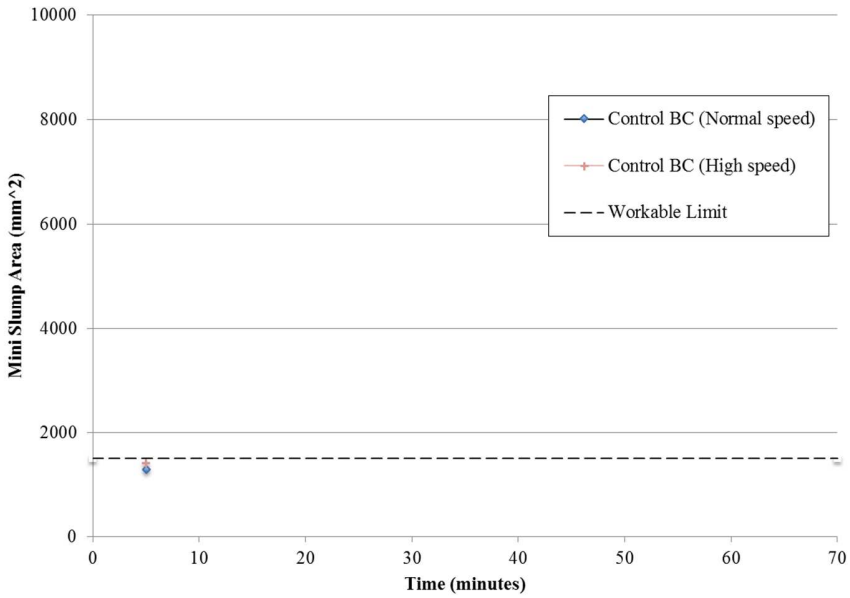

Figure 3.19: Effect of mixing intensity on mini slump area of BC fly ash geopolymer pastes without chemical admixtures

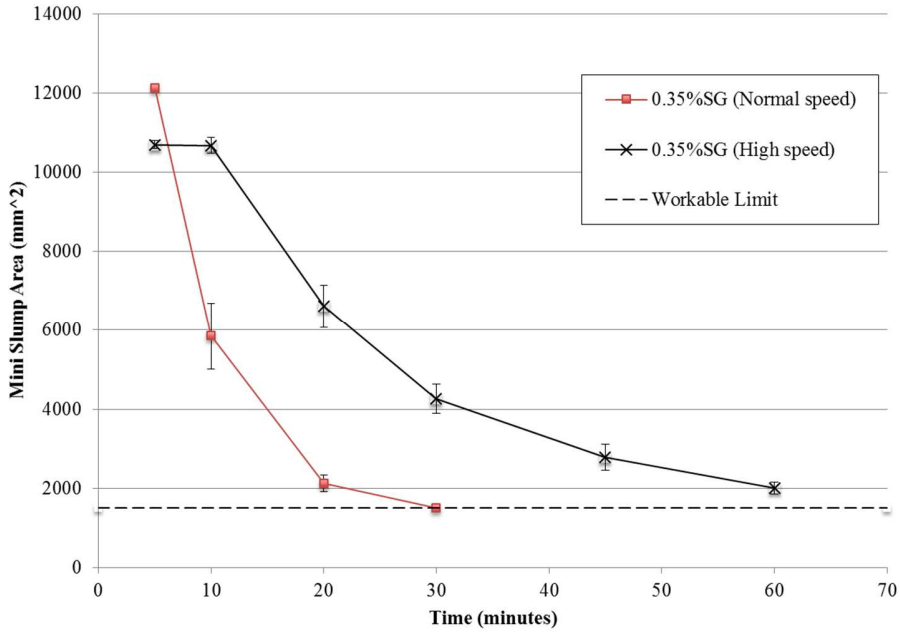

Figure 3.20: Effect of mixing intensity on mini slump area of BC fly ash geopolymer pastes with 0.35% sodium gluconate

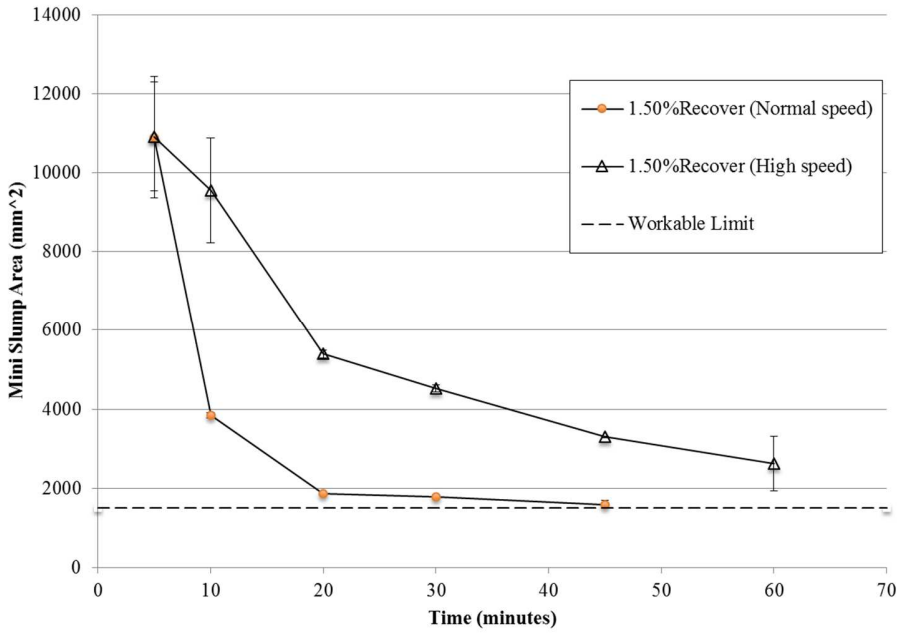

Figure 3.21: Effect of mixing intensity on mini slump area of BC fly ash geopolymer pastes with 1.50% Recover

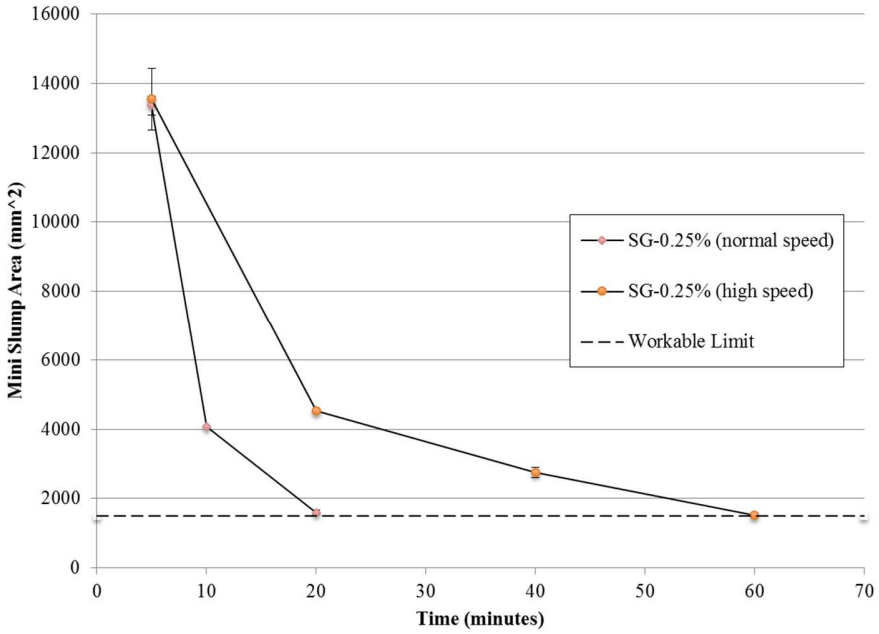

Figure 3.22: Effect of mixing intensity on mini slump area of MR fly ash geopolymer pastes with 0.25% sodium gluconate

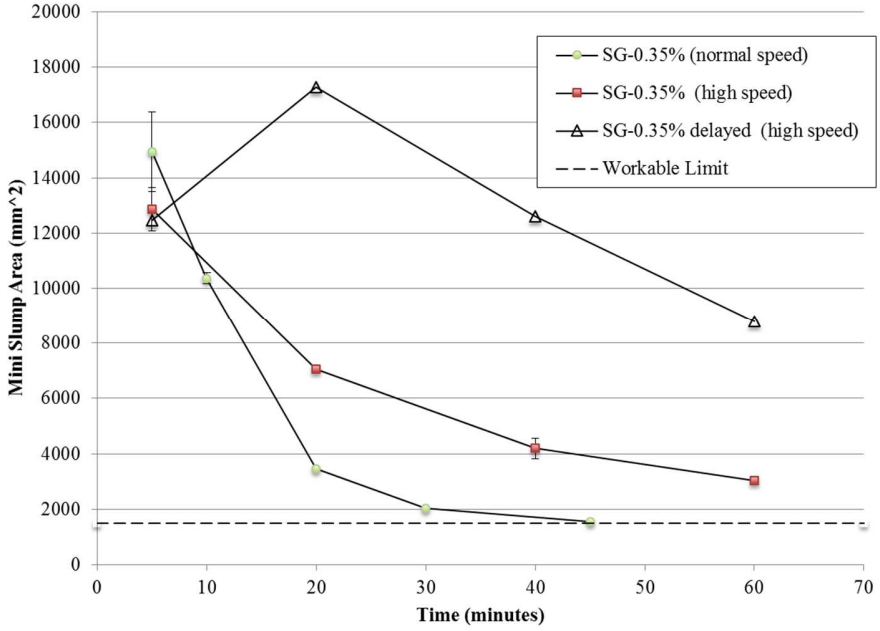

Figure 3.23: Effect of mixing intensity on mini slump area of MR fly ash geopolymer pastes with 0.35% sodium gluconate

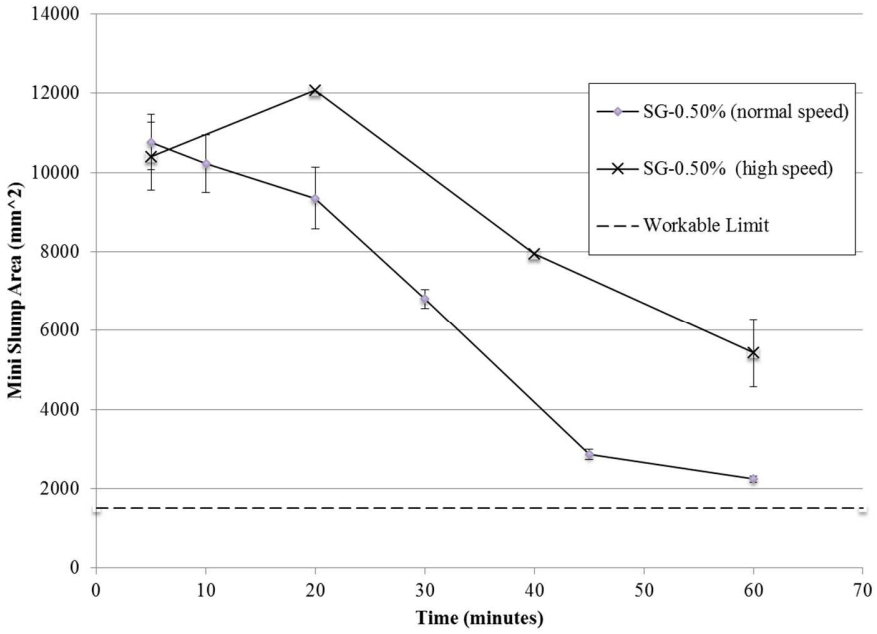

Figure 3.24: Effect of mixing intensity on mini slump area of MR fly ash geopolymer pastes with 0.50% sodium gluconate

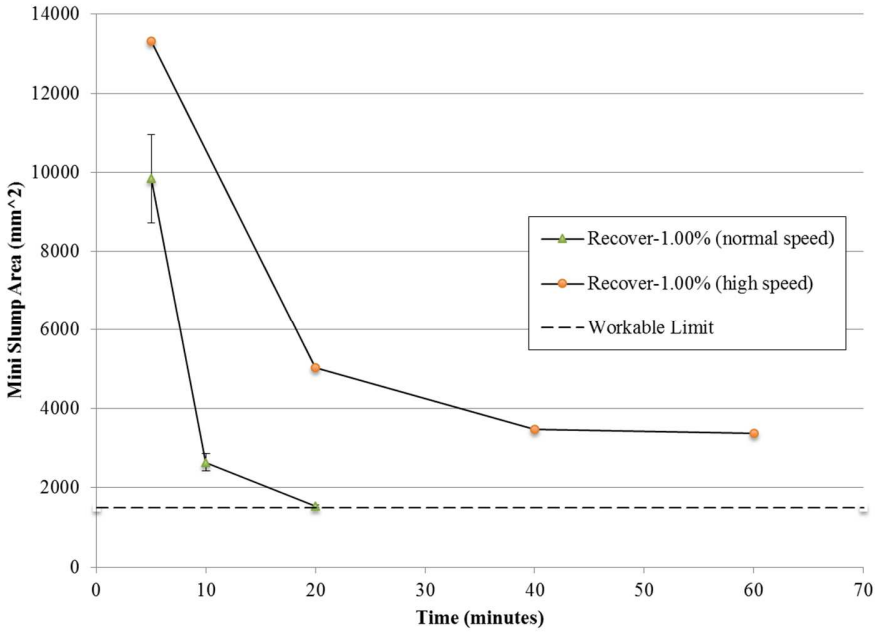

Figure 3.25: Effect of mixing intensity on mini slump area of MR fly ash geopolymer pastes with 1.00% Recover

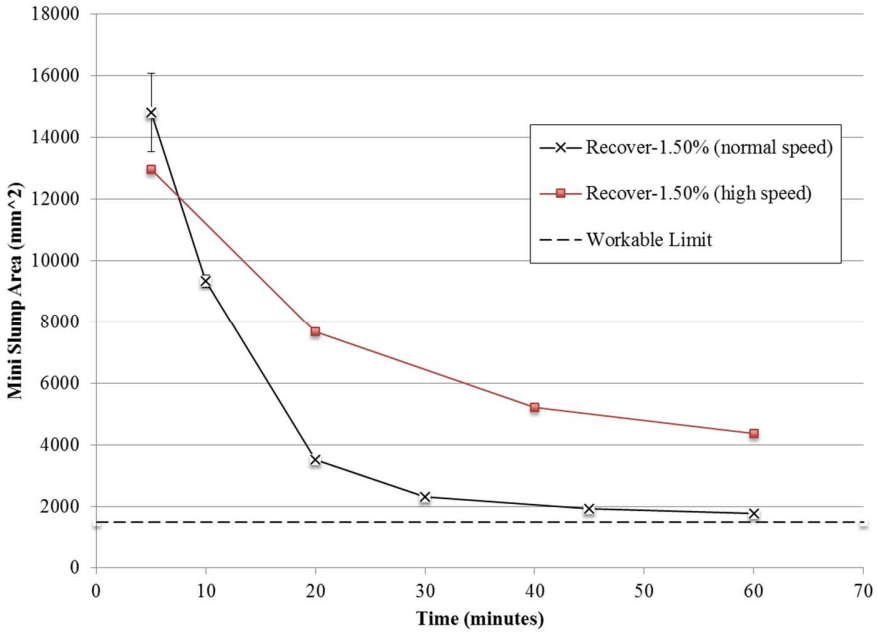

Figure 3.26: Effect of mixing intensity on mini slump area of MR fly ash geopolymer pastes with 1.50% Recover

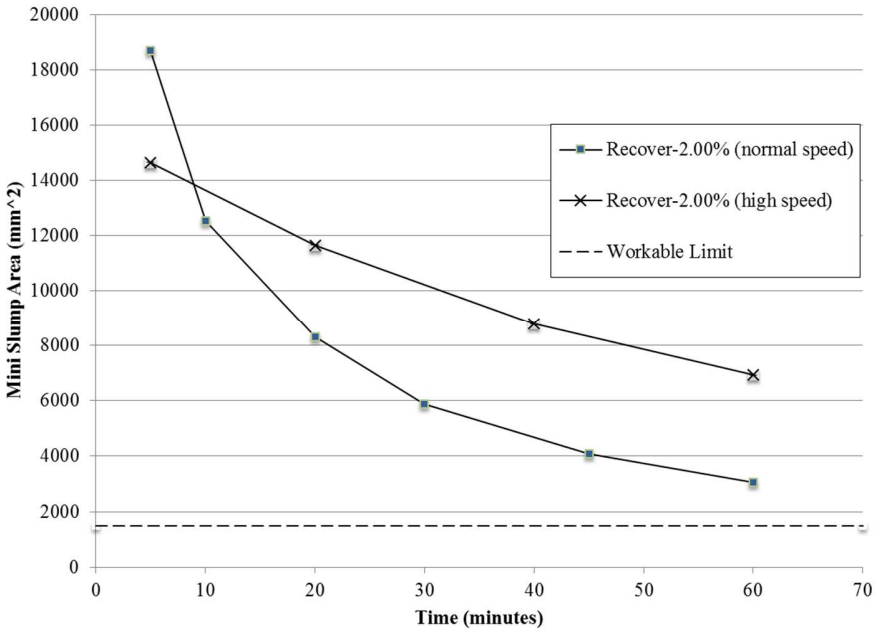

Figure 3.27: Effect of mixing intensity on mini slump area of MR fly ash geopolymer pastes with 2.00% Recover

3.6 Effect of fumed silica addition on mini slump loss of geopolymer pastes

In this section, fumed silica was added to the NaOH solution to obtain a molar ratio SiO_2/Na_2O of 1 (Ms = 1). For all fly ashes, the geopolymer pastes prepared with 4M NaOH solution (Ms = 1) exhibited high initial slump areas of 8900-12500 mm^2, even when no chemical admixtures were used; the results are shown in Figure 3.28. In addition, the pastes sustained high slump areas over 60 minutes of testing, and slight increases in slump areas were observed over the first 20 minutes for all fly ashes. For sodium gluconate and Recover additions, the MR fly ash geopolymer paste had the largest mini slump area compared to the other ashes, while the WP fly ash geopolymer paste had the largest mini slump area in the case of fumed silica addition. Since only silica modulus of 1 was studied, the system could be further optimized.

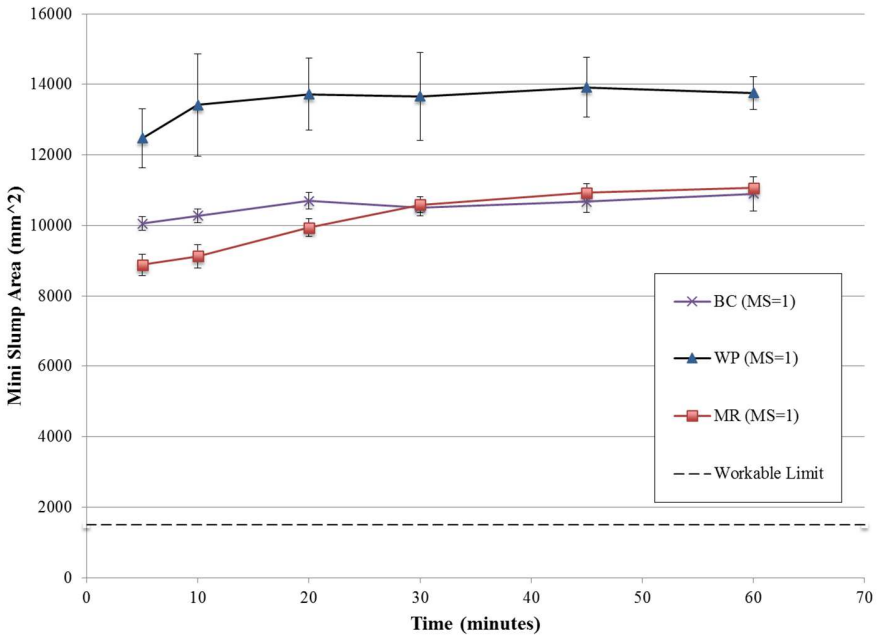

Figure 3.28: Mini slump area of geopolymer pastes with 4M NaOH (Ms=1)

3.7 Effect of sodium gluconate dosage on compressive strength of geopolymer pastes

While the addition of sodium gluconate improved mini slump flow of the geopolymer pastes, increasing the sodium gluconate dosage resulted in a drop in the compressive strength, as shown in Figures 3.29 and 3.30. With sodium gluconate dosages of 0.10% and 0.25%, the compressive strengths of the geopolymer pastes were comparable to or higher than the control pastes with no chemical admixtures for both 7 and 28 days. The increase in the compressive strength could be partially due to better consolidation of the specimens since the control paste cylinders always contained small cavities. With sodium gluconate dosages of 0.35% and 0.50%, the compressive strengths of the pastes at 7 and 28 days significantly decreased compared to the strengths of the control pastes. Therefore, sodium gluconate should not be added to geopolymer pastes at the dosages of more than 0.25% because it can cause a reduction in compressive strength of the paste. For the mixtures prepared by normal mixing conditions, that dosages greater than 0.25% reduced compressive strength is disappointing, since the optimum dosage for slump retention was determined to be 0.35%. However, it should be noted that the effect of sodium gluconate dosage on properties of geopolymers may change with the mixing conditions and type of slurry (e.g. paste, mortar, and concrete).

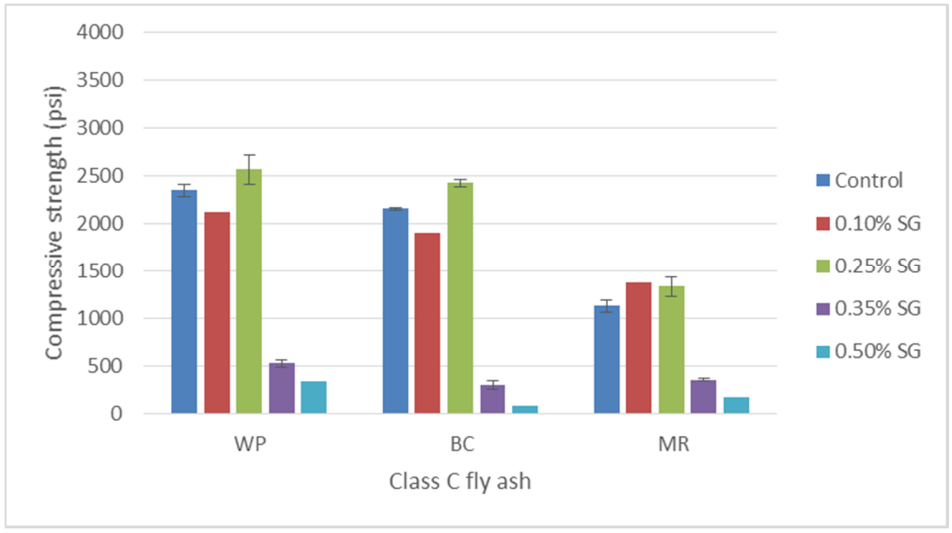

Figure 3.29: 7-day compressive strength of geopolymer pastes with sodium gluconate prepared using normal mixing conditions

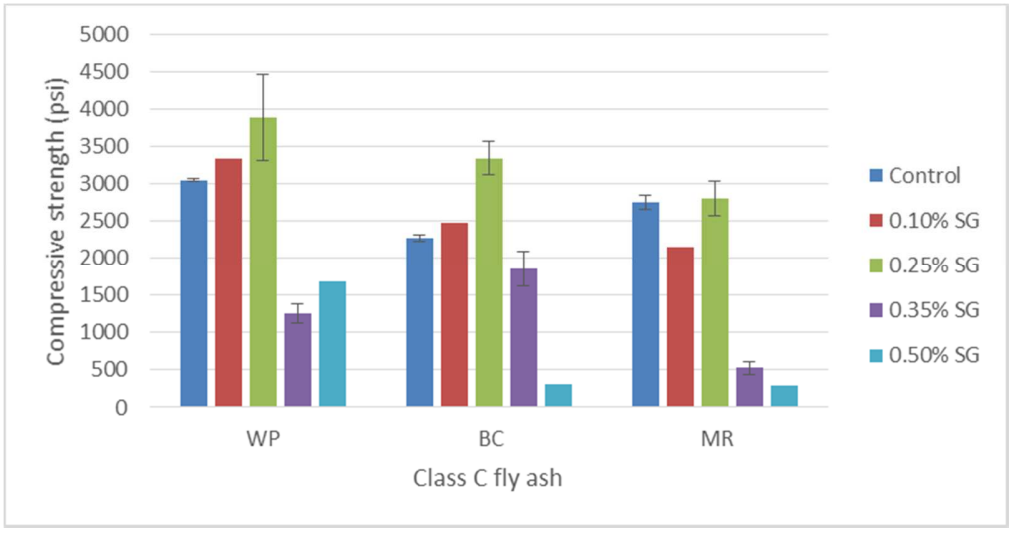

Figure 3.30: 28-day compressive strength of geopolymer pastes with sodium gluconate prepared using normal mixing conditions

3.8 Effect of Recover dosage on compressive strength of geopolymer pastes

The effect of Recover dosage on the compressive strength varied with the source of fly ash as shown in Figures 3.31-3.32, even though the fly ashes have similar chemical compositions. For a 1.00% addition of Recover, the compressive strengths of geopolymer paste made with BC fly ash were comparable to those of the control paste for both 7 and 28 days. Adding 1.00% Recover to the WP fly ash reduced strength by 28% at 7 days, but did not affect strength at 28 days. A 1.00% Recover addition reduced the strength of MR fly ash paste by approximately 60% at 7 and 28 days. Compressive strengths of the geopolymer pastes for all fly ashes decreased by 85-90% with 1.50% Recover. Consequently, an acceptable dosage of Recover for the fly ashes should be lower than 1.50% addition. This is in conflict with the mini slump tests, which suggested that Recover should be used at a 1.50% dosage to obtain good slump retention. Therefore, Recover may not be suitable when geopolymer pastes are prepared at low mixing speeds. As with sodium gluconate, this conflict suggests that Recover is not an appropriate admixture for slump retention because of the negative impact on compressive strength.

For sodium gluconate and Recover additions, geopolymer pastes made with MR fly ash tended to have lower compressive strengths than those made with BC and WP fly ashes, and fluctuations in loading rate were usually encountered during the mechanical testing of the specimens made with MR fly ash.

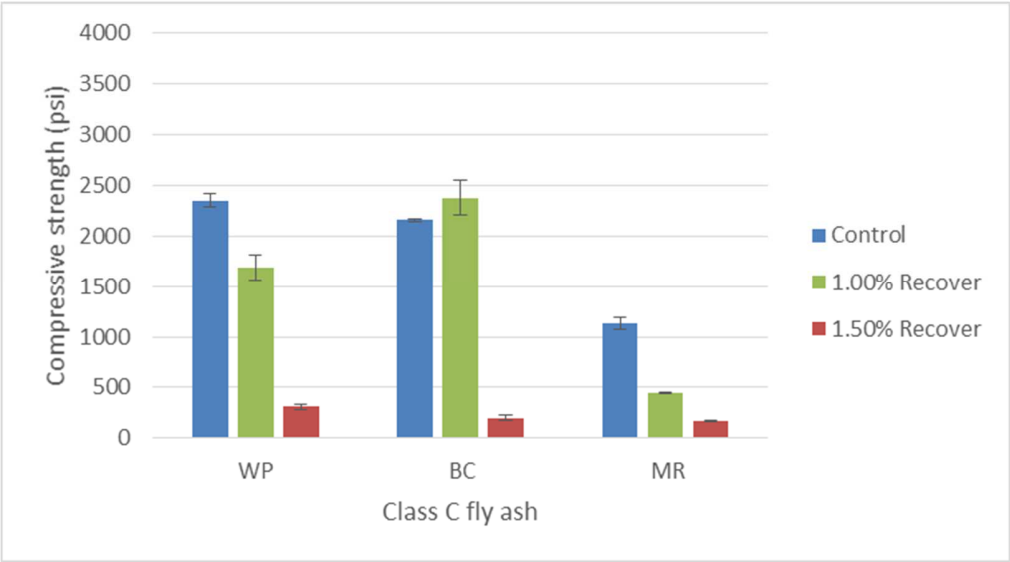

Figure 3.31: 7-day compressive strength of geopolymer pastes with Recover prepared using normal mixing conditions

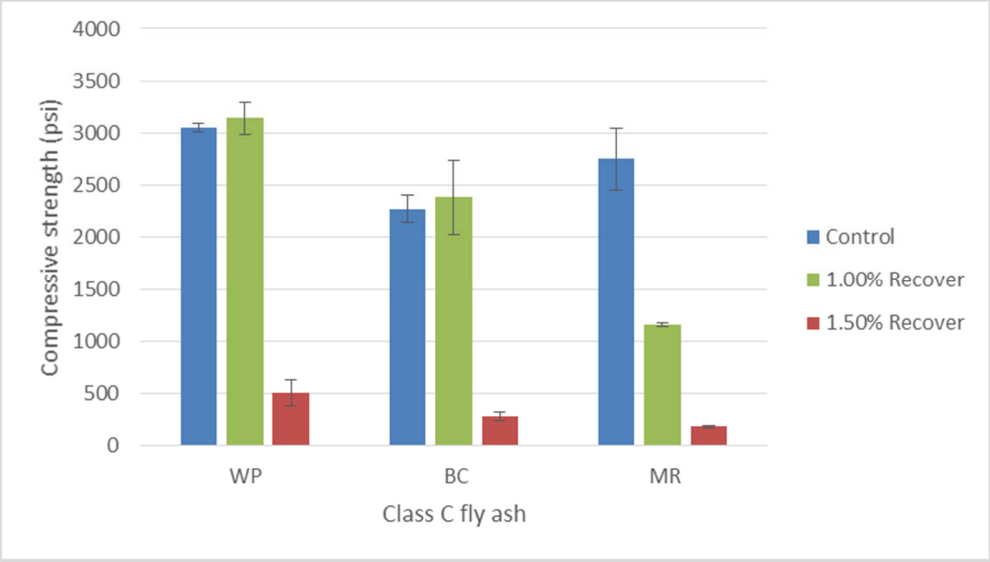

Figure 3.32: 28-day compressive strength of geopolymer pastes with Recover prepared using normal mixing conditions

3.9 Effect of chemical admixtures on compressive strength of portland cement paste

Sodium gluconate and Recover were also tested for the effect on compressive strength of portland cement paste and the results are presented in Figures 3.33-3.34. Sodium gluconate at 0.2% and Recover at 0.5% decreased the 7-day compressive strength by 75% and 60%, respectively. However, both admixtures resulted in 30% increase in 28-day strength. Although these dosages improved slump flow of the pastes with only slight bleeding for 0.2% sodium gluconate, significant drops in 7-day compressive strength should be considered if these chemical admixtures are used with portland cement.

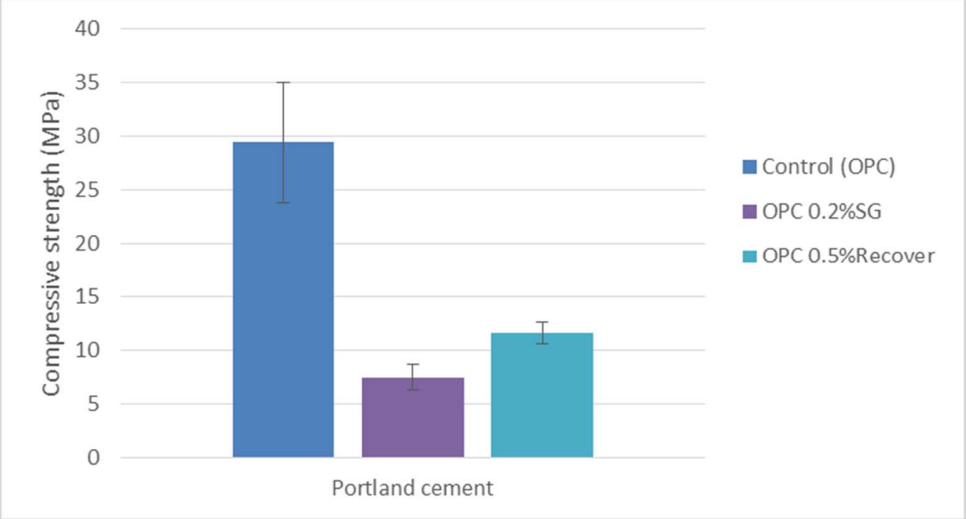

Figure 3.33: 7-day compressive strength of portland cement pastes prepared using normal mixing conditions

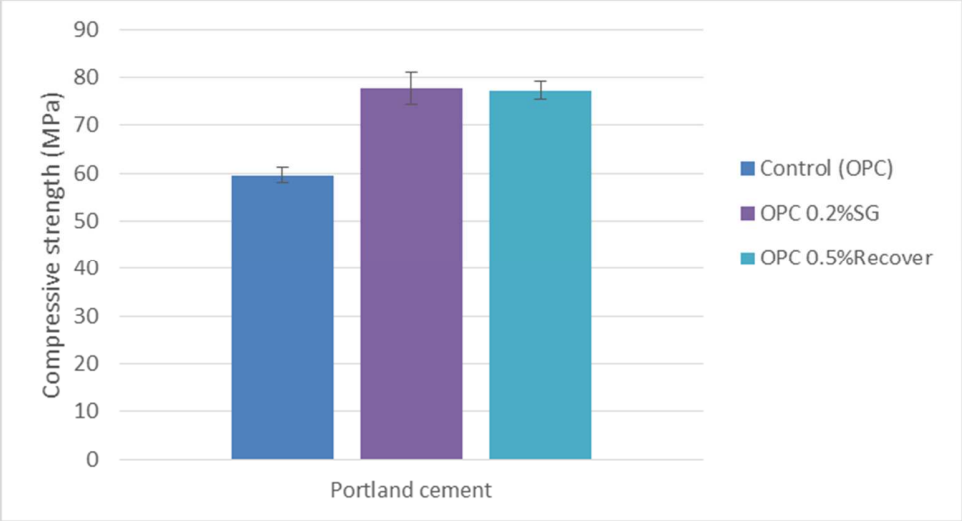

Figure 3.34: 28-day compressive strength of portland cement pastes prepared using normal mixing conditions

3.10 Effect of mixing intensity on compressive strength of geopolymer pastes

The effect of mixing intensity on compressive strength of geopolymer pastes is shown in Figures 3.35 and 3.36. The compressive strengths at 7 and 28 days of the pastes prepared by high shear mixing were mostly comparable to those of the pastes mixed by a planetary mixer. Increases in the compressive strength were obtained for 0.35% sodium gluconate at 7 days (140% increase) and 1.50% Recover at 28 days (173% increase) with high shear mixing. However, the strengths were still quite low compared to the control pastes. Although high shear mixing extended workable times of geopolymer pastes, it did not contribute to higher strengths of the pastes. For this compressive strength test, better consolidation of the specimens during sample preparation by high shear mixer was not achieved since the initial slump flows for both mixing procedures were not improved.

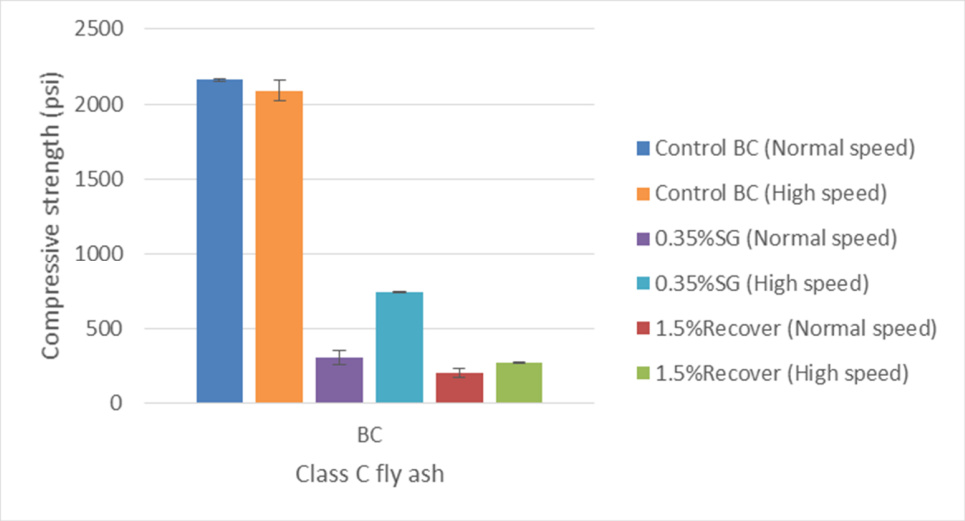

Figure 3.35: Effect of mixing intensity on 7-day compressive strength of BC fly ash geopolymer pastes

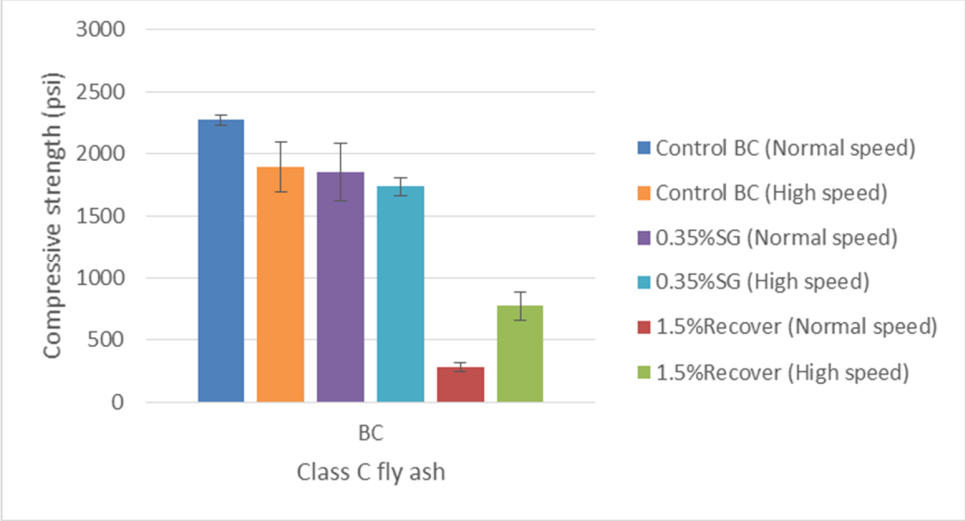

Figure 3.36: Effect of mixing intensity on 28-day compressive strength of BC fly ash geopolymer pastes

3.11 Effect of fumed silica addition on compressive strength of geopolymer pastes

Addition of fumed silica to NaOH solution as described in Section 2.1.3 significantly affected compressive strength of the geopolymer pastes. The compressive strengths of geopolymer pastes prepared with 4M NaOH (Ms = 1) solution were compared to the paste prepared with 4M NaOH solution without fumed silica as illustrated in Figures 3.37 and 3.38. The compressive strengths of the pastes at 7 days increased by about 30% for WP fly ash and 20% for BC fly ash, but decreased by about 90% for MR fly ash. The 28-day compressive strength increased by 80% for WP fly ash and 155% for BC fly ash, while it dropped by about 85% for MR fly ash. For WP and BC fly ashes, improvements in the compressive strengths of the paste were probably due to better consolidation of the specimens and increases in SiO_2/Al_2O_3 of the geopolymers [4]. For MR fly ash, the reason for the strength drops is unclear. However, soft surfaces of the paste specimens were observed during demolding and before the compressive strength tests at 7 and 28 days. This problem merits further investigation in the future. The addition of fumed silica to achieve an Ms of 1, therefore, is not a robust method of improving slump retention for geopolymer pastes.

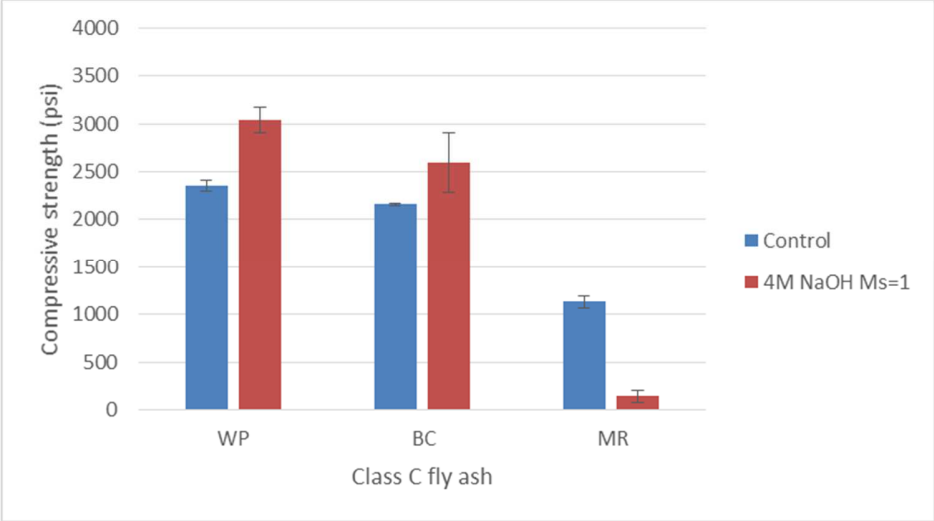

Figure 3.37: Effect of fumed silica addition on 7-day compressive strength of geopolymer pastes prepared using normal mixing conditions

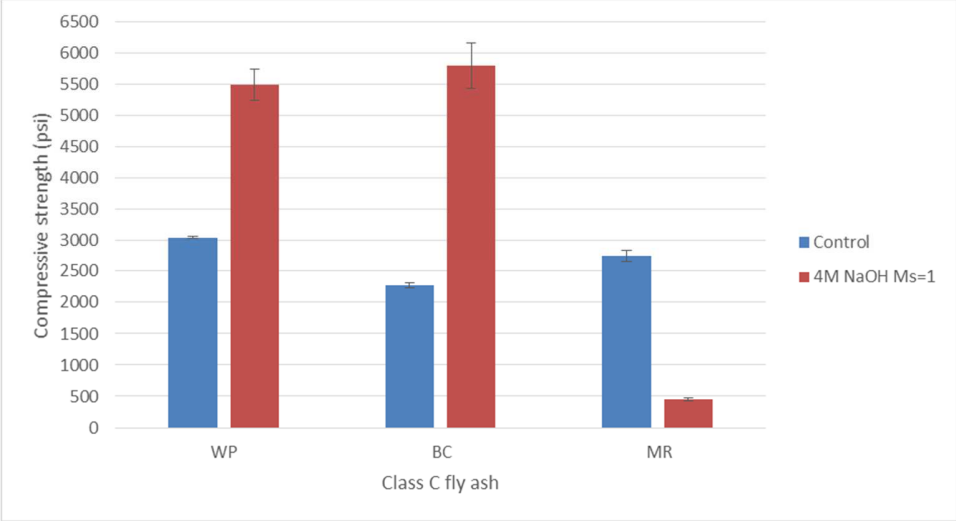

Figure 3.38: Effect of fumed silica addition on 28-day compressive strength of geopolymer pastes prepared using normal mixing conditions

3.12 Workability results

In this section, MR fly ash was used to test for rheological properties of geopolymer pastes. The geopolymer pastes were prepared using a high shear mixer, and a solution-to-powder ratio of 0.45 was used for all specimens. The workability of fresh geopolymer pastes was characterized by rheological testing and the mini slump loss test at 5, 20, 40, and 60 minutes after mixing the fly ash with NaOH solution. Using 0.25% to 0.50% sodium gluconate by mass of fly ash, the initial mini slump areas were 10000-13000 mm^2 (equivalent to average diameters of 115-132 mm) and the mini slump areas at 60 minutes were greater than the workable limit of 1500 mm^2 (43.70-mm diameter).

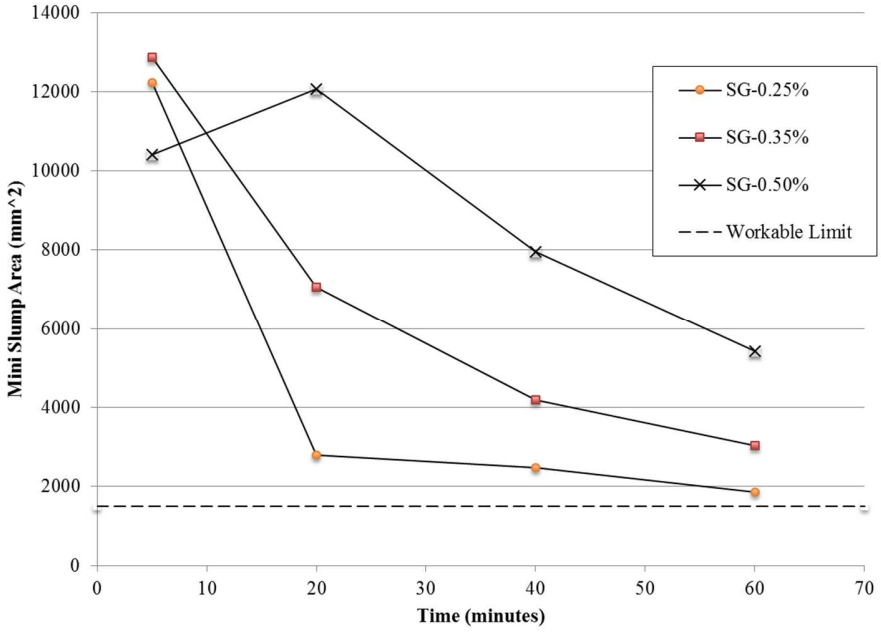

Figure 3.39: Mini slump area of MR fly ash geopolymer pastes with sodium gluconate

For the rotational rheometer results, the shear stress values were plotted with time for the entire shear rate protocol. Since the last ten data points of shear stress values

approaching the end of each shear rate for test segment 9 to 13 did not vary much, the average value can be considered the steady-state shear stress value at those particular shear rates. For each sample, the average shear stresses at different shear rates were plotted and a Bingham equation was determined using linear regression. From the Bingham equation, $\tau = \tau_0 + \mu\dot{\gamma}$, the y-intercept is the yield stress (τ_0) and the slope is the viscosity (μ) in the shear stress vs. shear rate plot [22]. Plots of the average shear stress as a function of shear rate (i.e., the flow curve) for geopolymer pastes with different dosages of sodium gluconate are shown in Appendix B.

The yield stresses and viscosities of the pastes containing sodium gluconate are summarized Table 3.1. Use of sodium gluconate at higher dosages reduced the yield stress of the geopolymer pastes. Yield stress is inversely proportional to slump (slump flow) [24, 25], thus the reduction in yield stress indicates that sodium gluconate improved workability of the geopolymer pastes by reducing the yield stress. The yield stress for all pastes increased with time as the pastes hardened. However, lower yield stress values did not necessarily indicate greater mini slump areas. For example, the paste with 0.50% sodium gluconate had considerably lower yield stress than the paste with 0.25% sodium gluconate at 5 minutes, but the mini slump area was relatively smaller. For the effect on viscosity, typically the pastes with 0.35% and 0.50% sodium gluconate had lower viscosities than the paste with 0.25% sodium gluconate. The yield stress and viscosity values for the paste with 0.25% sodium gluconate at 40 and 60 minutes in Table 3.1 were left blank since the pastes lost their workability rapidly after remixing and this was observed after the rheometer test as shown in Figure 3.40. The yield stress of the paste with 0.25% at 40 minutes was greater

than those of the paste at 5 and 20 minutes, however a negative value of viscosity was obtained for the test, thus invalidating the analysis. In addition, retesting of the paste at 40 minutes resulted in different stress values at the same shear rate as shown in Figure 3.41.

Table 3.1: Yield stress and viscosity for the paste containing sodium gluconate

Sample age	Rheological Parameters of MR fly ash containing sodium gluconate					
	MR 0.25% SG		MR 0.35% SG		MR 0.50% SG	
	Yield stress (Pa)	Viscosity (Pa·s)	Yield stress (Pa)	Viscosity (Pa·s)	Yield stress (Pa)	Viscosity (Pa·s)
5 min	132	1.48	37	0.39	19	0.88
20 min	278	1.17	99	0.30	26	0.19
40 min	-	-	142	0.29	76	0.37
60 min	-	-	227	0.61	100	0.40

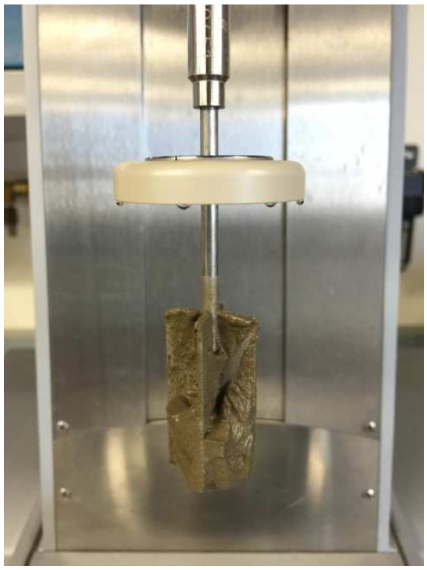

Figure 3.40: Geopolymer paste with 0.25% sodium gluconate after rheometer measurement at 40 minutes

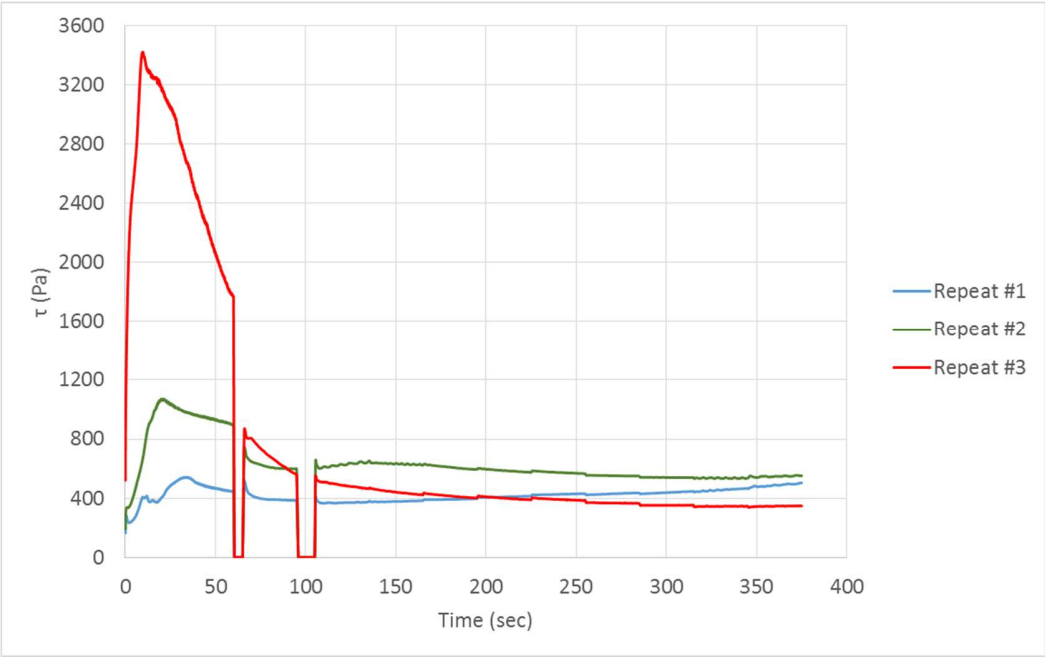

Figure 3.41: Stress vs. time plot for paste with 0.25% sodium gluconate at 40 minutes for 3 different measurements

With respect to delayed addition of admixture, the addition of sodium gluconate at the dosages of 0.25% and 0.35% increased the mini slump areas of the geopolymer pastes at 20, 40, and 60 minutes compared to the pastes with the same dosages by the normal addition, 100-240% for 0.25% addition and 150-220% for 0.35% addition. Interestingly, delayed addition did not affect the initial slump areas (Figure 3.42). Therefore, delayed addition of sodium gluconate can be used as a means to improve the workability retention without an impact on initial properties. Plots of average shear stress as a function of shear rate for geopolymer paste with delayed additions of 0.25% and 0.35% sodium gluconate are shown in Appendix B.

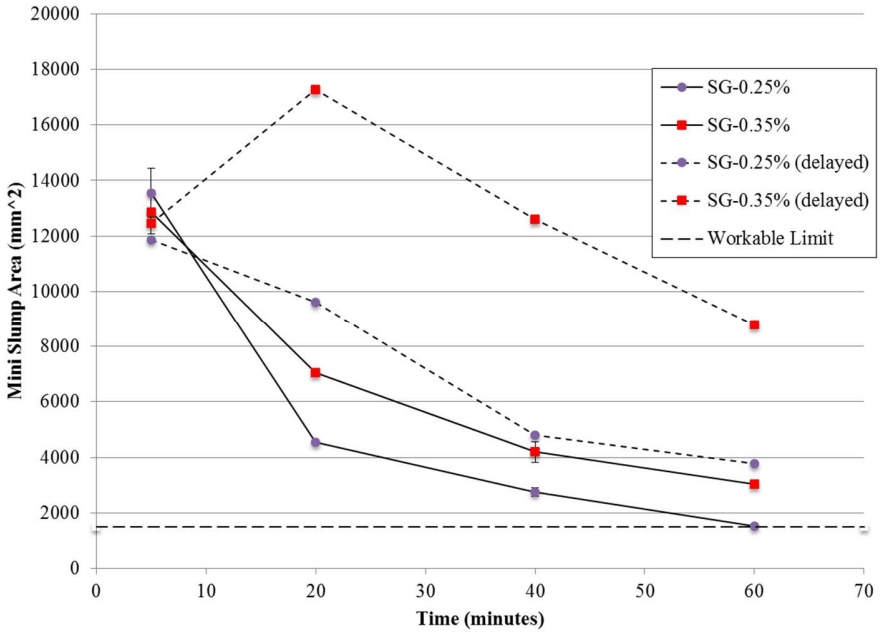

Figure 3.42: Mini slump area of MR fly ash geopolymer pastes with delayed addition of sodium gluconate

The yield stress and viscosity of the samples obtained from the Bingham model are summarized Table 3.2. Compared to normal addition, the delayed additions of 0.25% and 0.35% sodium gluconate reduced the yield stress of the pastes by approximately 80-90%, while the viscosities were also changed by -20% to 100% with respect to the controls. However, the delayed addition of 0.25% and 0.35% sodium gluconate resulted in clumps of fly ash particles present in the pastes as shown in Figure 3.44, which were not observed in the pastes prepared by normal addition of the admixture as shown in Figure 3.43. Use of higher mixing intensity and reduction in delayed addition time possibly eliminated the floc formation, resulting in an improved dispersion of fly ash particles. These flocs might improve workability of the pastes by increasing the effective solution-to-powder ratio since

the surface area of the particles has been reduced, thus increasing the amount of free solution available. Presence of the clumps of fly ash particles interfered with the rheometer measurement as the stress value fluctuated over the entire period for all measurements (5, 20, 40, and 60 minutes); high jumps of the shear stress value were removed before calculating the average shear stress. A plot of stress vs. time for the paste with delayed addition of 0.25% sodium gluconate at 5 minutes is shown in Figure 3.45.

Table 3.2: Yield stress and viscosity for the paste with delayed addition of sodium gluconate

Sample age	Rheological Parameters of MR fly ash containing sodium gluconate			
	MR 0.25% SG (delayed)		MR 0.35% SG (delayed)	
	Yield stress (Pa)	Viscosity (Pa·s)	Yield stress (Pa)	Viscosity (Pa·s)
5 min	15	1.48	5	0.71
20 min	65	1.41	8	0.60
40 min	141	0.85	24	0.58
60 min	194	0.98	53	0.48

Figure 3.43: Geopolymer paste with 0.25% sodium gluconate at 5 minutes

Figure 3.44: Geopolymer paste with delayed addition of 0.25% sodium gluconate at 5 minutes

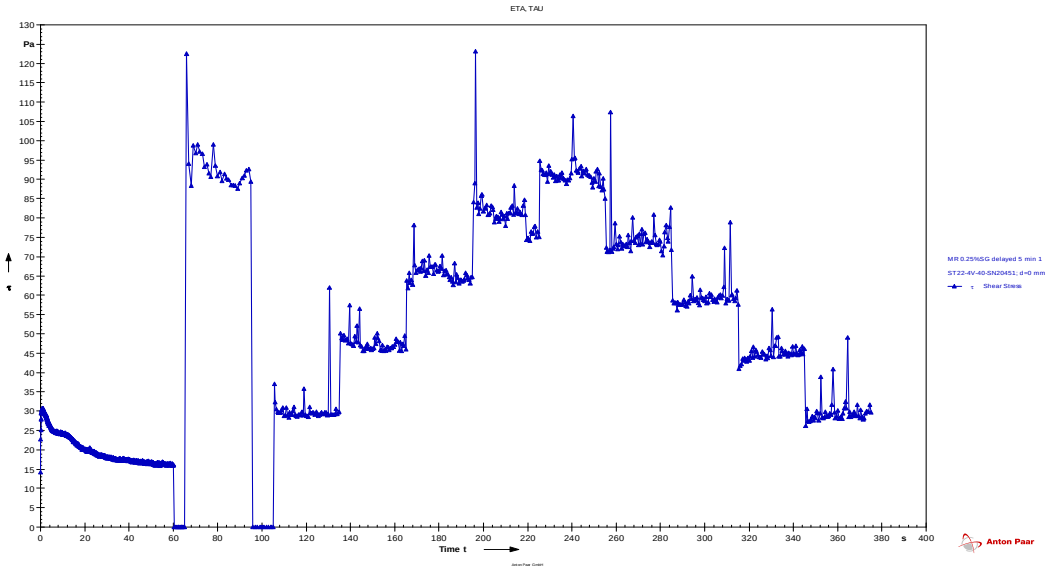

Figure 3.45: Stress vs. time plot for paste with delayed addition of 0.25% sodium gluconate at 5 minutes

Using 1.00% to 2.00% Recover by mass of the fly ash, the initial mini slump areas of the geopolymer pastes were about 13000-15000 mm^2 (130-140 mm in diameters) which were greater than those of the pastes containing 0.25% to 0.50% sodium gluconate. For all Recover dosages, the mini slump areas at 60 minutes were greater than the workable limit. At 20, 40, and 60 minutes, greater increases in the mini slump area were obtained when increasing Recover dosage from 1.50% to 2.00% (50-70% increase) compared to increasing the dosage from 1.00% to 1.50% (30-50% increase). Plots of average shear stress as a function of shear rate for geopolymer pastes containing different dosages of Recover are shown in Appendix B.

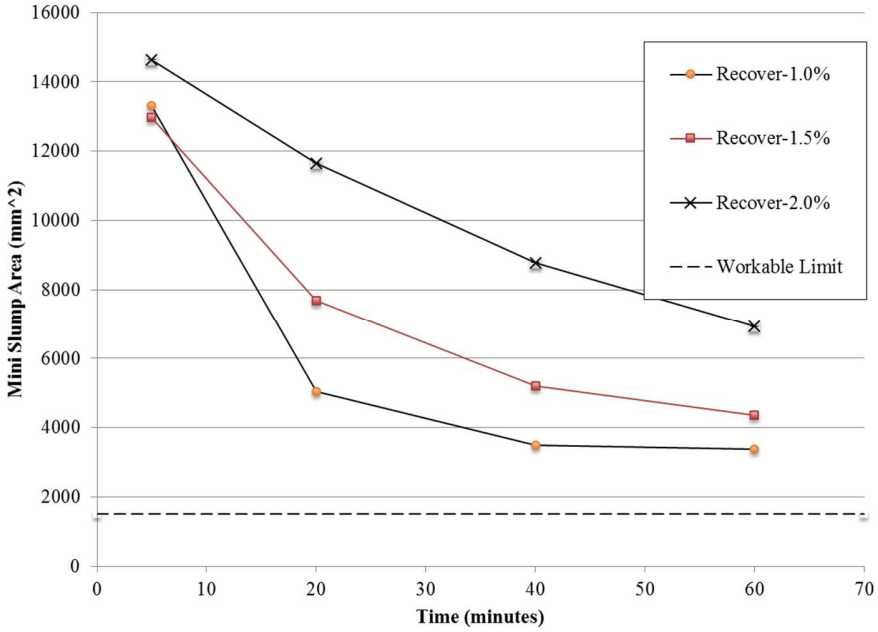

Figure 3.46: Mini slump area of MR fly ash geopolymer pastes with Recover

The yield stresses and viscosities of the pastes containing Recover are summarized Table 3.3. Addition of Recover resulted in an improved workability of the geopolymer pastes by reducing both the yield stress and the viscosity. With increasing Recover dosage, reductions in the yield stress were observed for all measurements, while decreases in the viscosity were achieved at 20, 40, and 60 minutes. Furthermore, there was no problem of rapid stiffening of the pastes at 40 and 60 minutes for all dosages of Recover that were tested. This could be attributed to the difference in the admixture dosages employed and the impact this had on slump retention. In addition, the mini slump area at 60 minutes of the paste containing 1.00% Recover was greater than 3300 mm^2 which is well above the workable limit, while the mini slump areas of paste with 0.25% sodium gluconate at 40 and 60 minutes were only about 2400 and 1800 mm^2, respectively.

Table 3.3: Yield stress and viscosity for the paste containing Recover

Sample age	Rheological Parameters of MR fly ash containing Recover					
	MR 1.00% Recover		MR 1.50% Recover		MR 2.00% Recover	
	Yield stress (Pa)	Viscosity (Pa·s)	Yield stress (Pa)	Viscosity (Pa·s)	Yield stress (Pa)	Viscosity (Pa·s)
5 min	80	0.37	44	0.33	25	0.69
20 min	117	0.92	88	0.30	36	0.21
40 min	150	1.30	115	0.48	81	0.19
60 min	172	1.34	131	1.00	73	0.23

Although addition of fumed silica to the NaOH solution to obtain silica modulus of 1 (Ms = 1) contributed to a relatively lower initial mini slump area of the geopolymer paste at 5 minutes as compared to the pastes prepared with sodium gluconate, i.e. SG-0.35%, SG-0.50%, SG-0.35% (delayed) in Figure 3.47. The mini slump area of paste containing fumed silica, denoted as MR (Ms = 1), increased at 20 minutes, after which this paste maintained the mini slump areas in the range of about 10000 to 11000 mm^2 over 60 minutes as shown in Figure 3.47. In addition, the geopolymer paste prepared with fumed silica addition had the highest mini slump area at 60 minutes compared to all samples that have been tested. The flow curves for geopolymer pastes with fumed silica addition are shown in Appendix B.

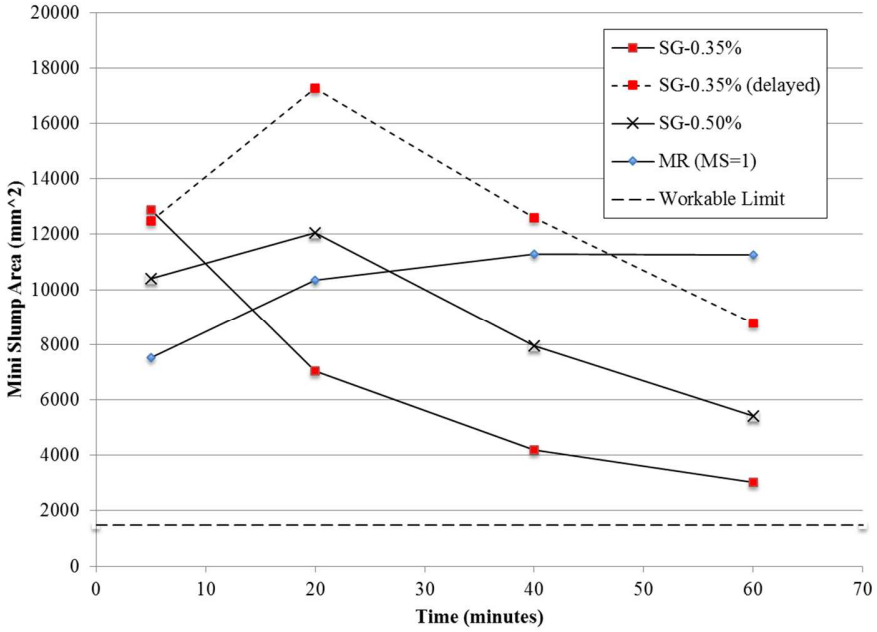

Figure 3.47: Mini slump area of geopolymer paste with fumed silica addition

The yield stresses and viscosities of the specimens containing fumed silica are summarized Table 3.4. The pastes prepared with fumed silica addition had comparatively low yield stresses and viscosities as compared to the pastes containing sodium gluconate and Recover. Similar to the mini slump area results from 20 to 60 minutes, the yield stress and viscosity of the paste were also unchanged over this time.

Table 3.4: Yield stress and viscosity for the paste with fumed silica addition

Sample age	MR fly ash with fumed silica addition	
	Yield stress (Pa)	Viscosity (Pa·s)
5 min	27	0.55
20 min	24	0.23
40 min	24	0.33
60 min	26	0.32

In summary, mini slump area, yield stress, and viscosity of geopolymer pastes obtained from different methods of workability improvement at 5 and 60 minutes are compared in Figures 3.48-3.50. While comparable initial mini slump areas of 12000-13000 mm^2 were achieved from 0.35% additions of sodium gluconate (normal and delayed additions) and 1.50% addition of Recover, the paste prepared with delayed addition of sodium gluconate retained the greatest mini slump area at 60 minutes among these samples, followed by Recover addition and sodium gluconate addition, respectively. The geopolymer paste prepared with fumed silica addition had the smallest mini slump area at 5 minutes, but the greatest mini slump area at 60 minutes compared to those prepared from other methods of workability improvement. For the effect on yield stress, delayed addition of sodium gluconate provided the lowest yield stress (5 Pa) at 5 minutes, but fumed silica addition contributed to relatively low yield stresses at 5 and 60 minutes (27 and 26 Pa, respectively). At 60 minutes, the yield stress values were inversely related to the mini

slump areas. Viscosity values of the pastes were ranged from 0.32 to 1.00 Pa·s and the values did not correlate with the mini slump areas or the yield stresses.

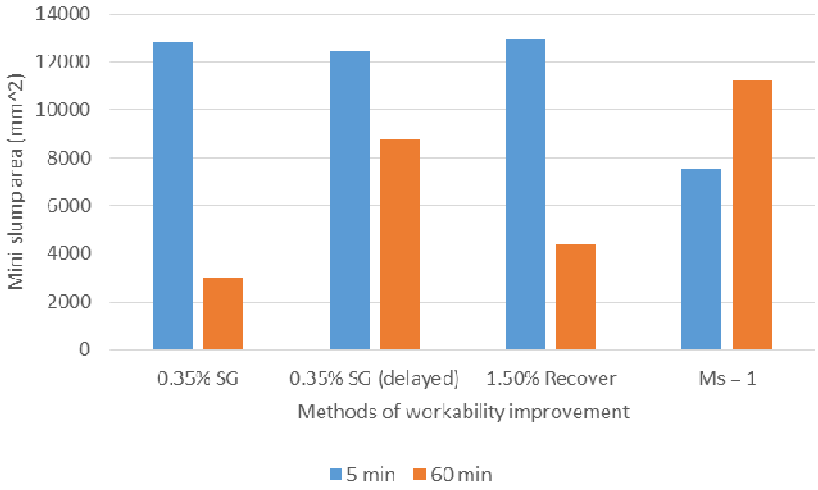

Figure 3.48: Mini slump area of geopolymer pastes from different methods of workability improvement

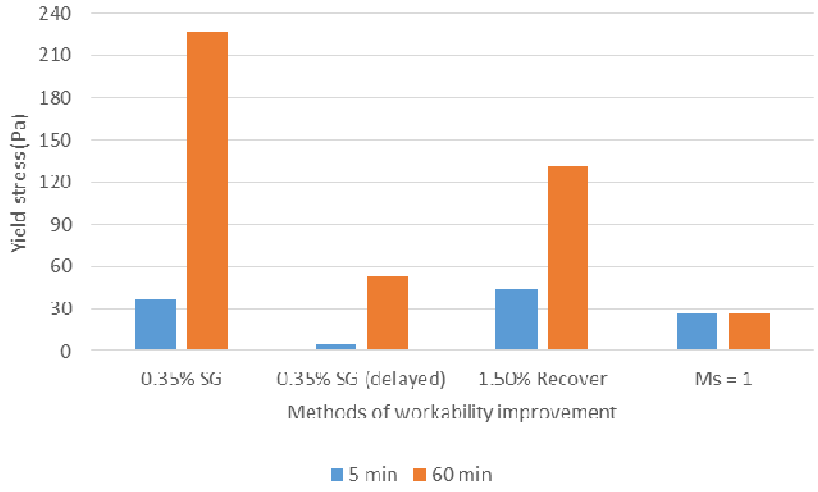

Figure 3.49: Yield stress of geopolymer pastes from different methods of workability improvement

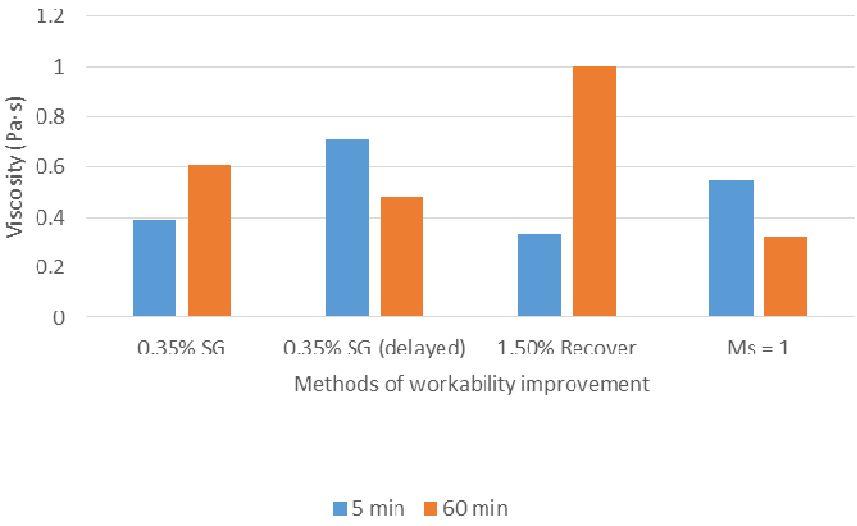

Figure 3.50: Viscosity of geopolymer pastes from different methods of workability improvement

Chapter 4: Conclusions and Suggestions for Future Work

4.1 Conclusions

In this study, the effect of chemical admixtures on properties of high-calcium fly ash geopolymers was investigated. The main findings obtained from the study are as follows:

- Sodium gluconate and Recover improved the workability of the geopolymer pastes. From the mini slump loss results, the optimum dosages for sodium gluconate and Recover were 0.35% and 1.50% by mass of fly ash, respectively, when the paste was mixed using a mixer as prescribed in ASTM C305. These additions allowed workable times of at least 30 minutes. However, additions of sodium gluconate and Recover at the optimum dosages resulted in reductions in compressive strength of the geopolymer pastes compared to the pastes without chemical admixtures when prepared using a planetary mixer. For the same dosage of sodium gluconate and Recover, the slump areas of MR fly ash geopolymer pastes were greatest, followed by those of WP and BC fly ashes, respectively.
- Other chemical admixtures including borax (sodium tetraborate decahydrate), Sikament N (naphthalene sulfonate), and sodium sulfate did not improve the workability of geopolymer pastes, and the initial slump areas of the geopolymer pastes containing those chemical admixtures were less than the workable limit of 1500 mm^2.

- Portland cement paste without chemical admixtures retained workable slump at 60 minutes. Additions of sodium gluconate and Recover increased the mini slump area of the paste, but an excess amount caused bleeding. The optimum dosages of sodium gluconate and Recover were considered to be 0.20% and 0.75%, respectively, since these dosages resulted in increased initial slump areas and only slight bleeding. The optimum dosage of Recover is within the range of the manufacturer's recommended use. However, additions of 0.20% sodium gluconate and 0.50% Recover resulted in significant drops in the 7-day compressive strength.
- High shear mixing prolonged workable times of geopolymer pastes, but it did not always increase the initial slump areas. In addition, high shear mixing did impact the compressive strength of some specimens.
- For fumed silica addition, the geopolymer pastes prepared with NaOH (Ms = 1) solution sustained large mini slump areas for over 60 minutes for all fly ashes. The fumed silica addition increased the compressive strengths for WP and BC fly ashes, but resulted in significant drops in the strengths for MR fly ash.
- Yield stress of the geopolymer paste could be reduced by adding sodium gluconate, Recover, and fumed silica. For sodium gluconate addition, the yield stress was also further reduced by delayed addition of the admixture.

4.2 Suggestions for future work

- The results of fumed silica addition were helpful, but not conclusive. Since the effect on compressive strength varied with the sources of fly ash, the causes of strength drops for the MR fly ash geopolymer paste should be investigated. In

addition, Ms of the NaOH solution other than 1 should be tested for the effects on mini slump loss and compressive strength as the mini slump areas at 60 minutes were significantly larger than those from other methods of workability improvement.

- Delayed addition of sodium gluconate could allow the geopolymer paste to achieve comparable mini slump area with lower dosage of the admixture compared to the normal mixing procedure. However, the effect of delayed addition on compressive strength needs to be tested.
- Higher mixing intensity (higher than 1000 rpm) should be tested to determine the effect on compressive strength, mini slump area, elimination of floc formation from a delayed addition of a chemical admixture.

Appendix A: Stress Plots of MR Fly Ash Geopolymer Pastes

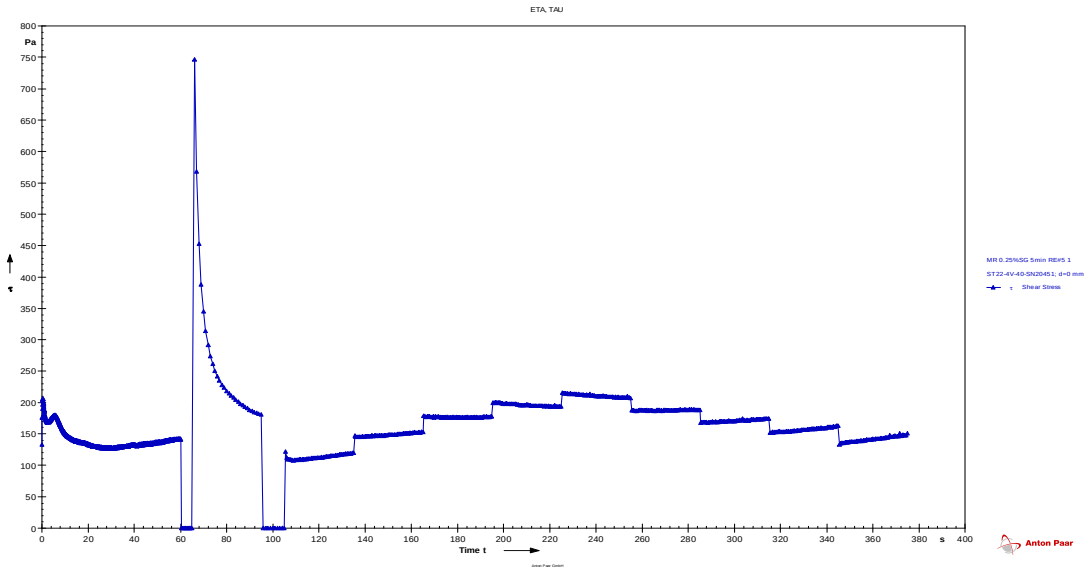

Figure A.1: Stress vs. time plot for the paste with 0.25% sodium gluconate at 5 minutes

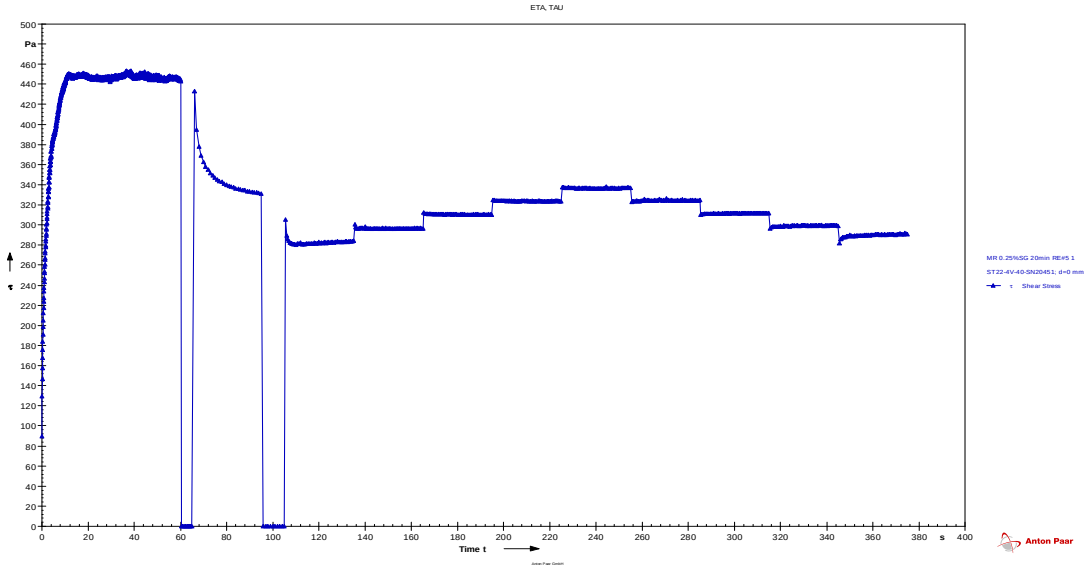

Figure A.2: Stress vs. time plot for the paste with 0.25% sodium gluconate at 20 minutes

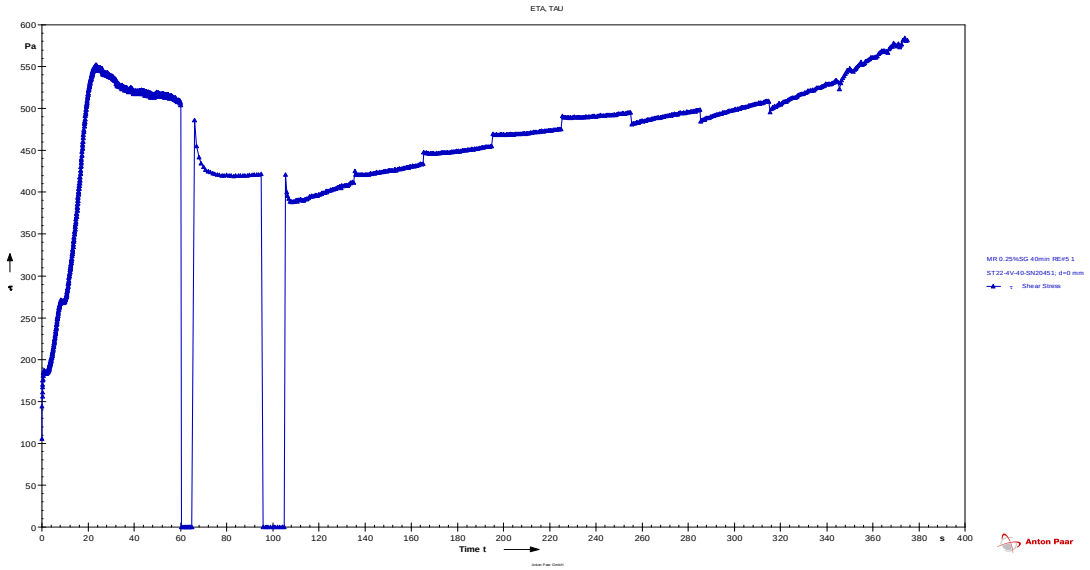

Figure A.3: Stress vs. time plot for the paste with 0.25% sodium gluconate at 40 minutes

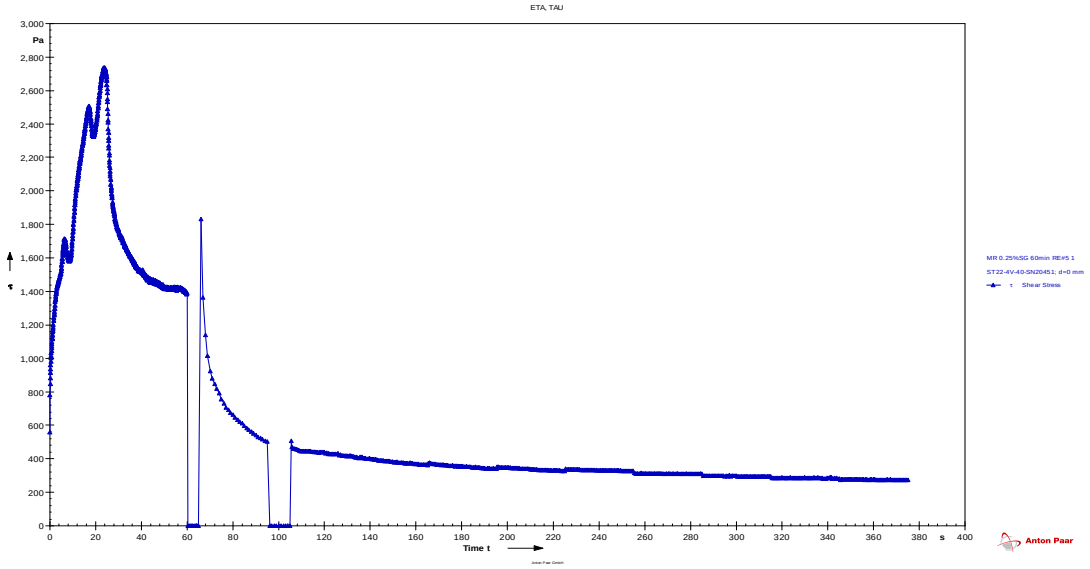

Figure A.4: Stress vs. time plot for the paste with 0.25% sodium gluconate at 60 minutes

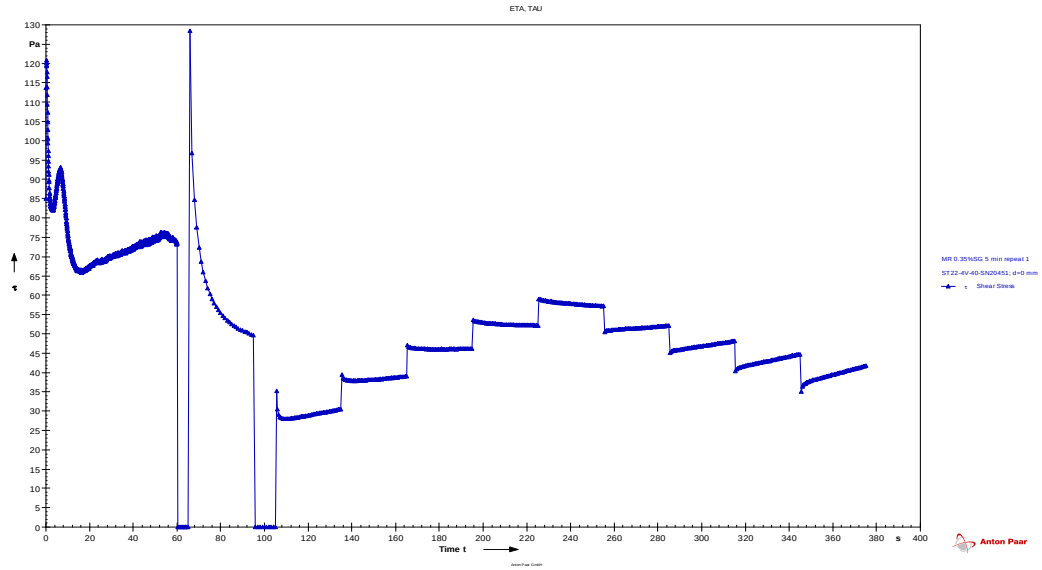

Figure A.5: Stress vs. time plot for the paste with 0.35% sodium gluconate at 5 minutes

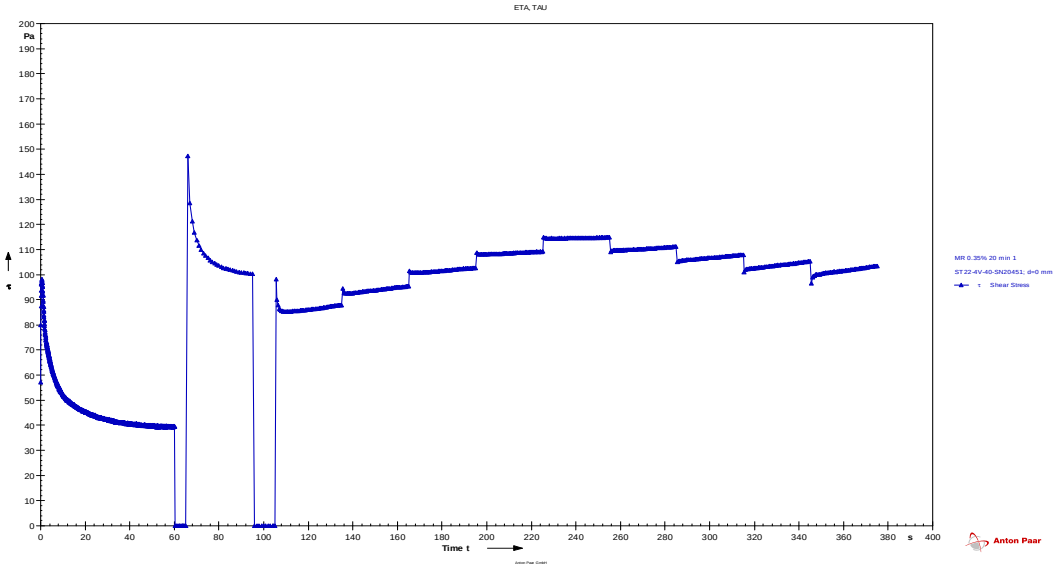

Figure A.6: Stress vs. time plot for the paste with 0.35% sodium gluconate at 20 minutes

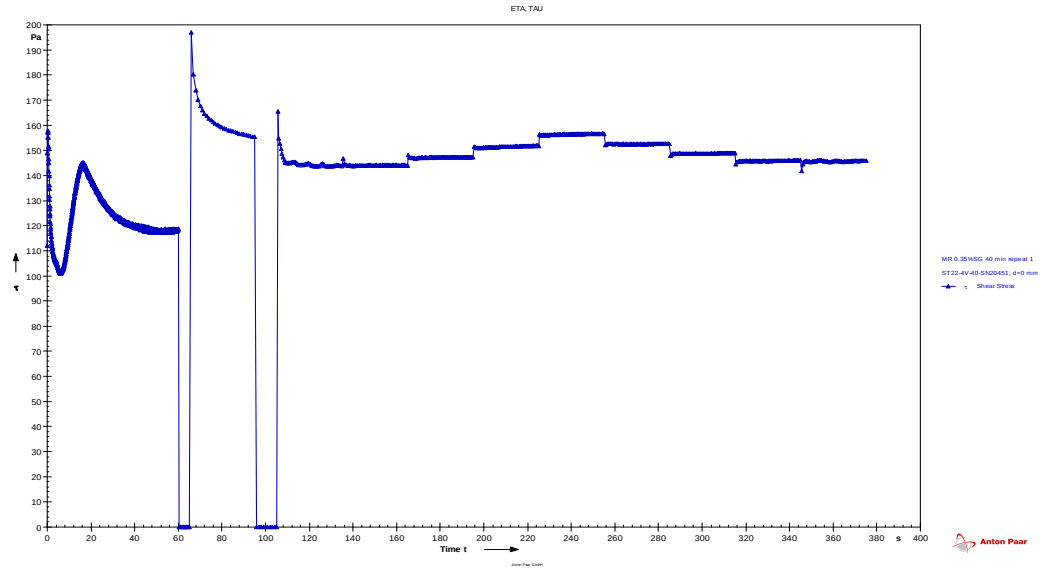

Figure A.7: Stress vs. time plot for the paste with 0.35% sodium gluconate at 40 minutes

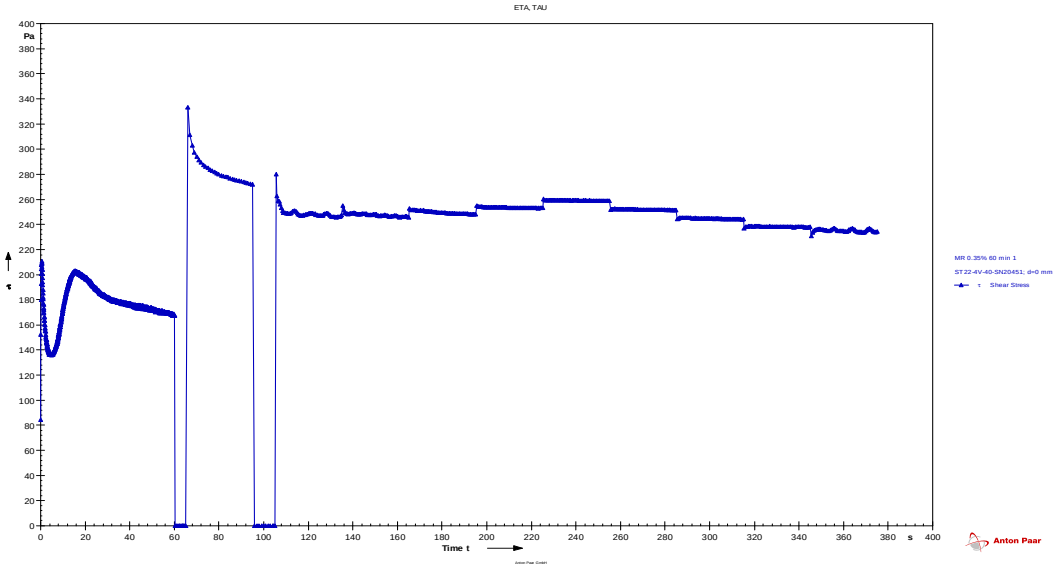

Figure A.8: Stress vs. time plot for the paste with 0.35% sodium gluconate at 60 minutes

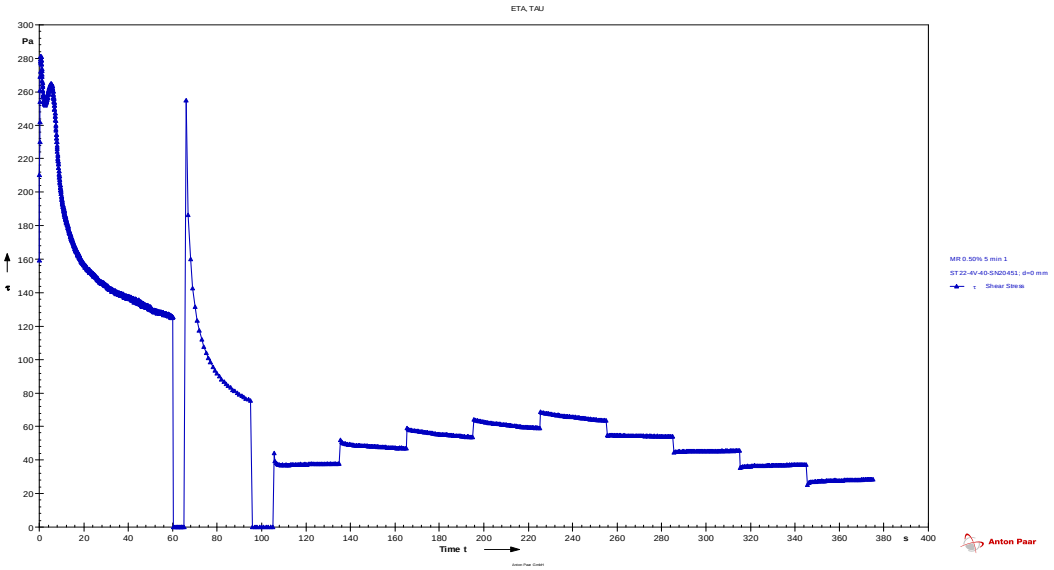

Figure A.9: Stress vs. time plot for the paste with 0.50% sodium gluconate at 5 minutes

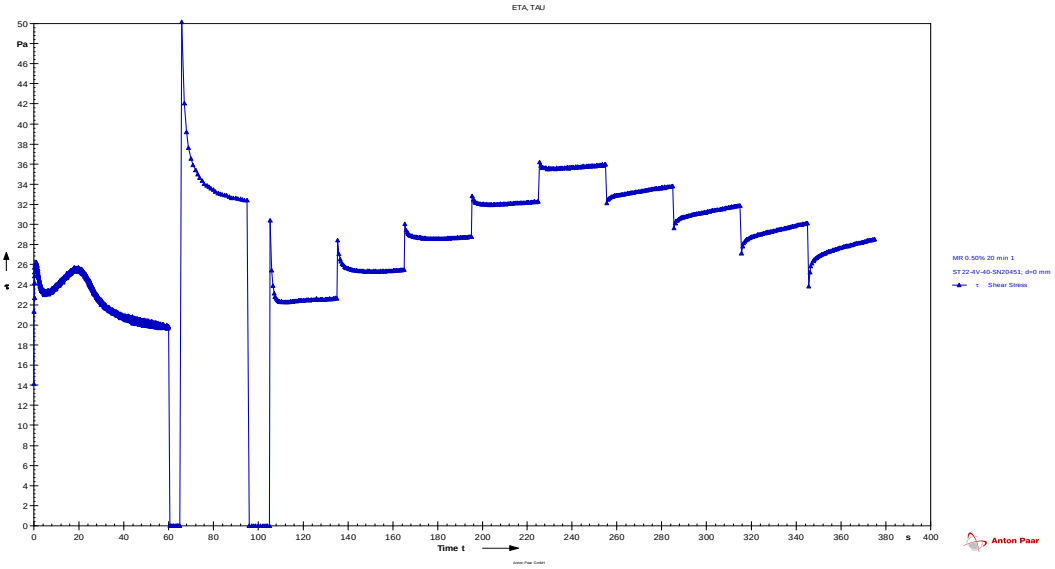

Figure A.10: Stress vs. time plot for the paste with 0.50% sodium gluconate at 20 minutes

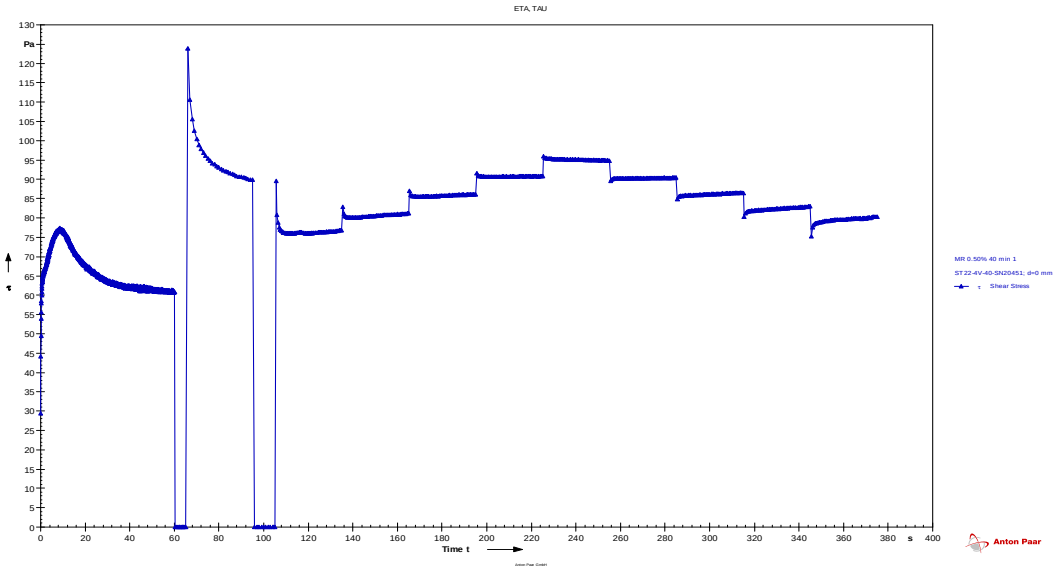

Figure A.11: Stress vs. time plot for the paste with 0.50% sodium gluconate at 40 minutes

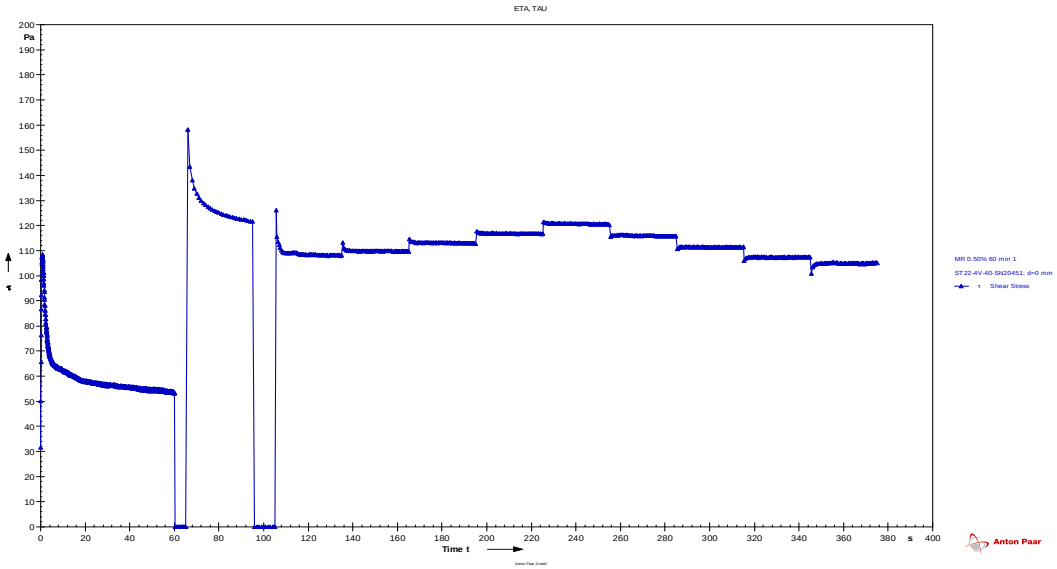

Figure A.12: Stress vs. time plot for the paste with 0.50% sodium gluconate at 60 minutes

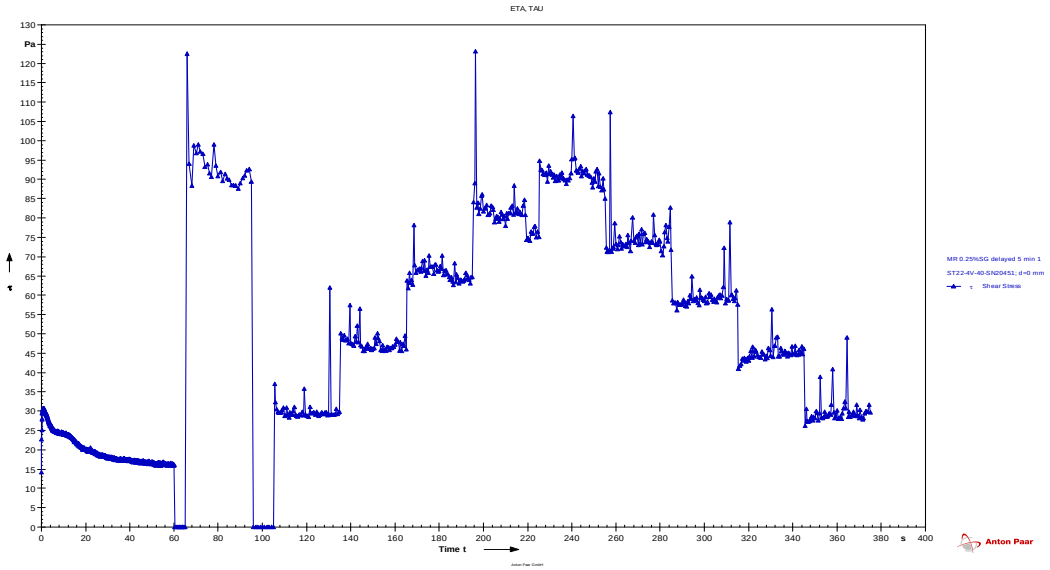

Figure A.13: Stress vs. time plot for the paste with delayed addition of 0.25% sodium gluconate at 5 minutes

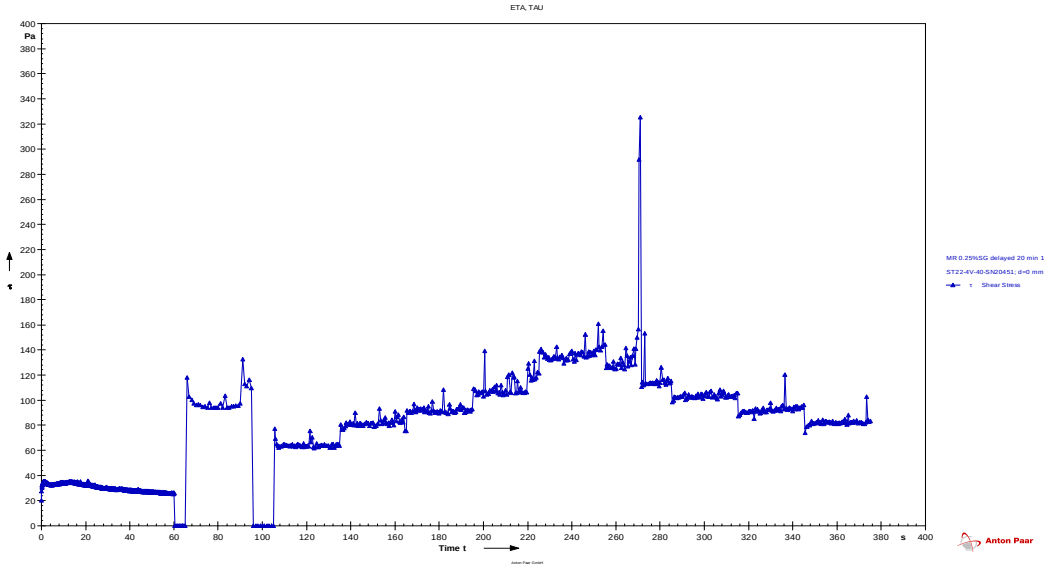

Figure A.14: Stress vs. time plot for the paste with delayed addition of 0.25% sodium gluconate at 20 minutes

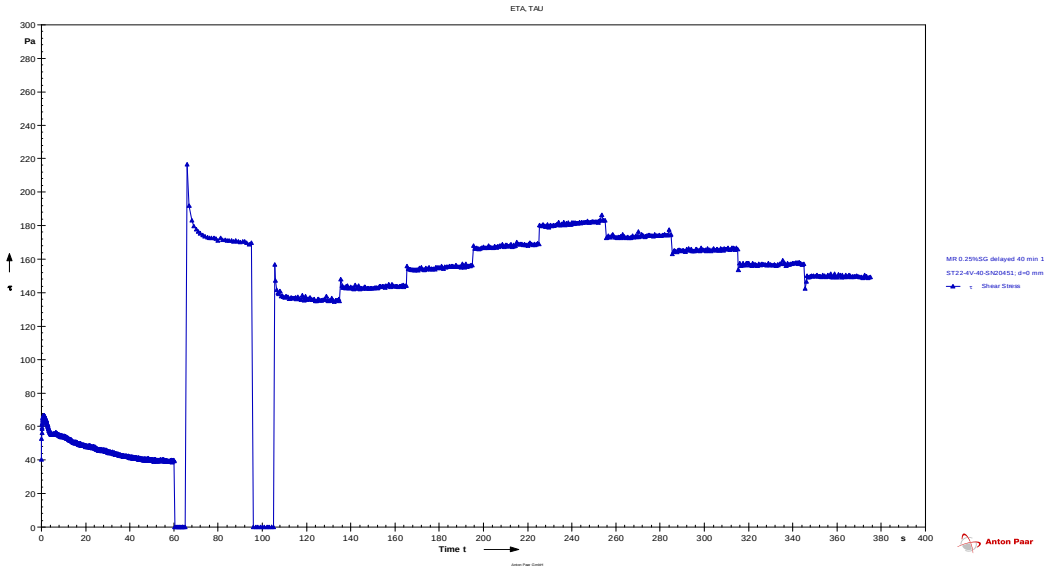

Figure A.15: Stress vs. time plot for the paste with delayed addition of 0.25% sodium gluconate at 40 minutes

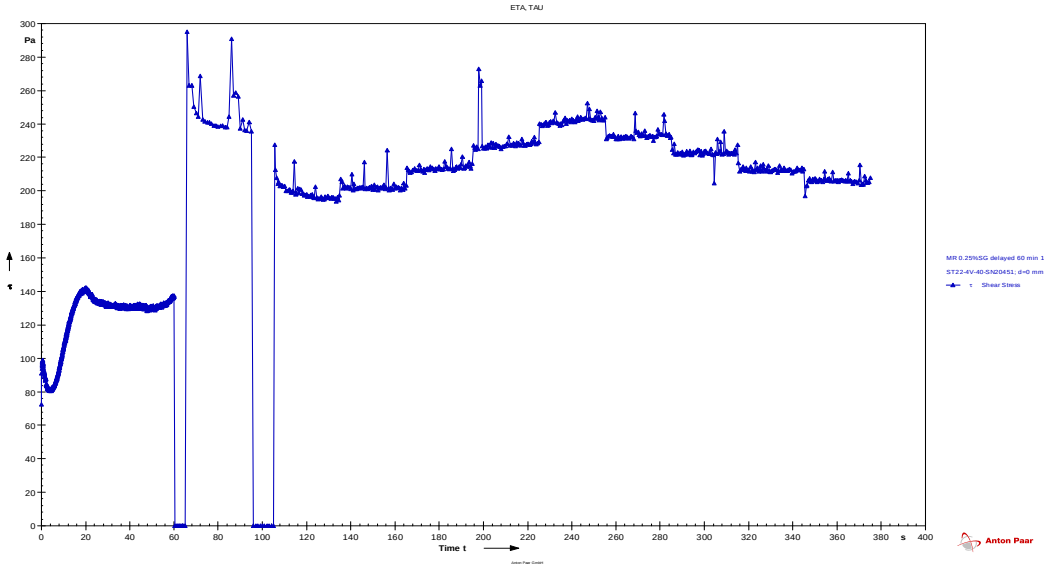

Figure A.16: Stress vs. time plot for the paste with delayed addition of 0.25% sodium gluconate at 60 minutes

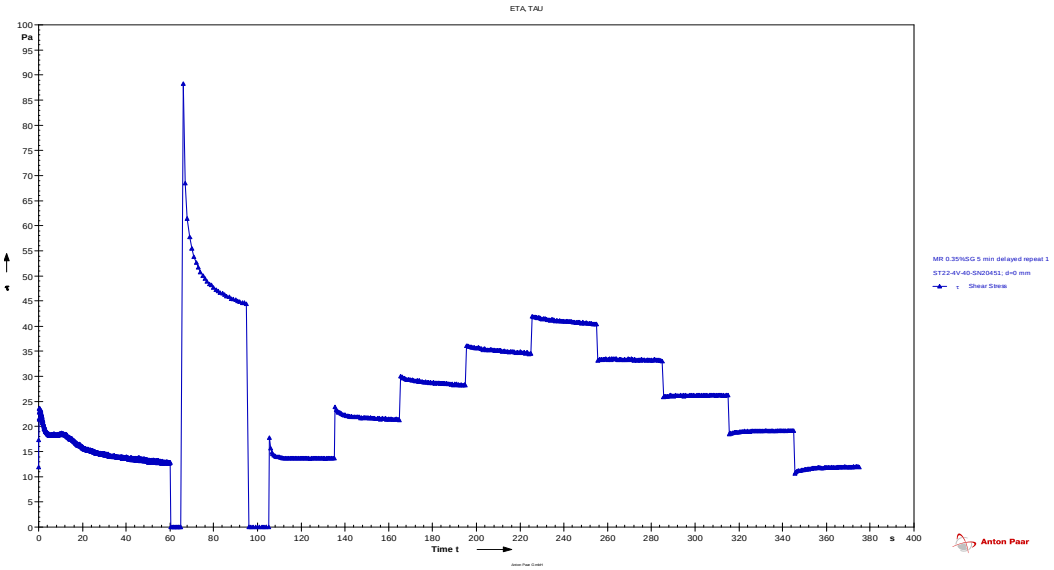

Figure A.17: Stress vs. time plot for the paste with delayed addition of 0.35% sodium gluconate at 5 minutes

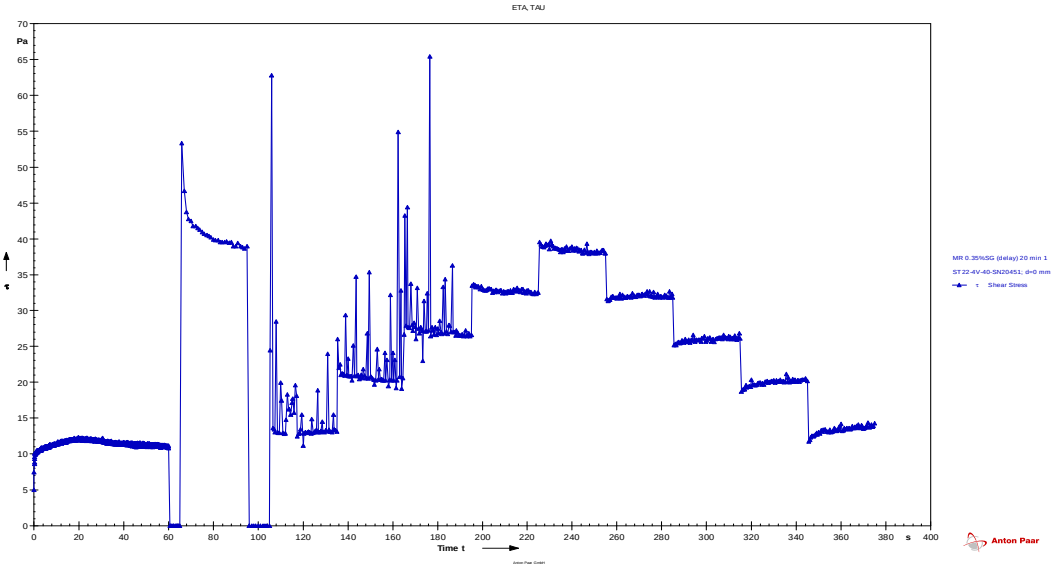

Figure A.18: Stress vs. time plot for the paste with delayed addition of 0.35% sodium gluconate at 20 minutes

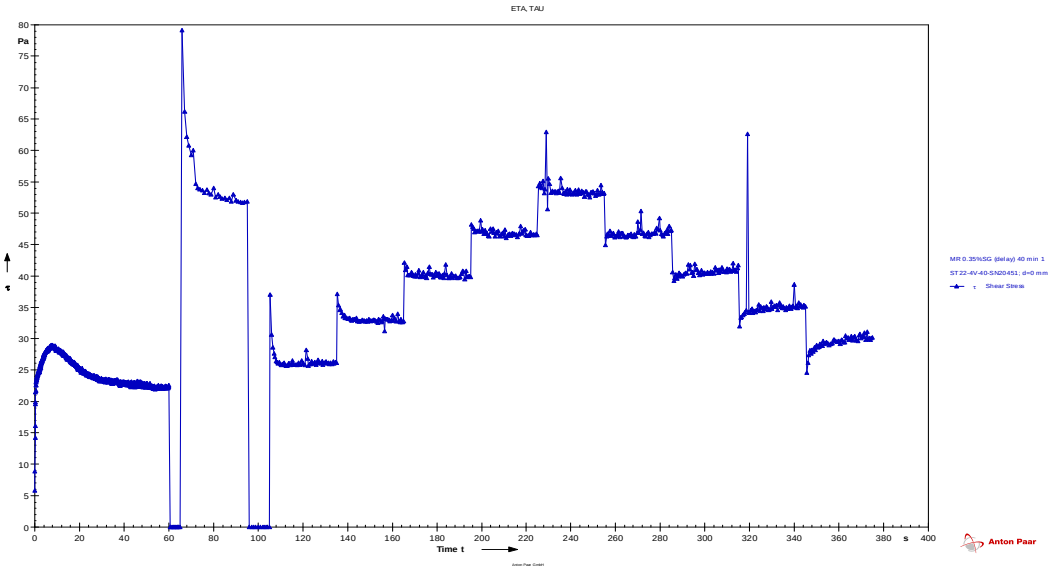

Figure A.19: Stress vs. time plot for the paste with delayed addition of 0.35% sodium gluconate at 40 minutes

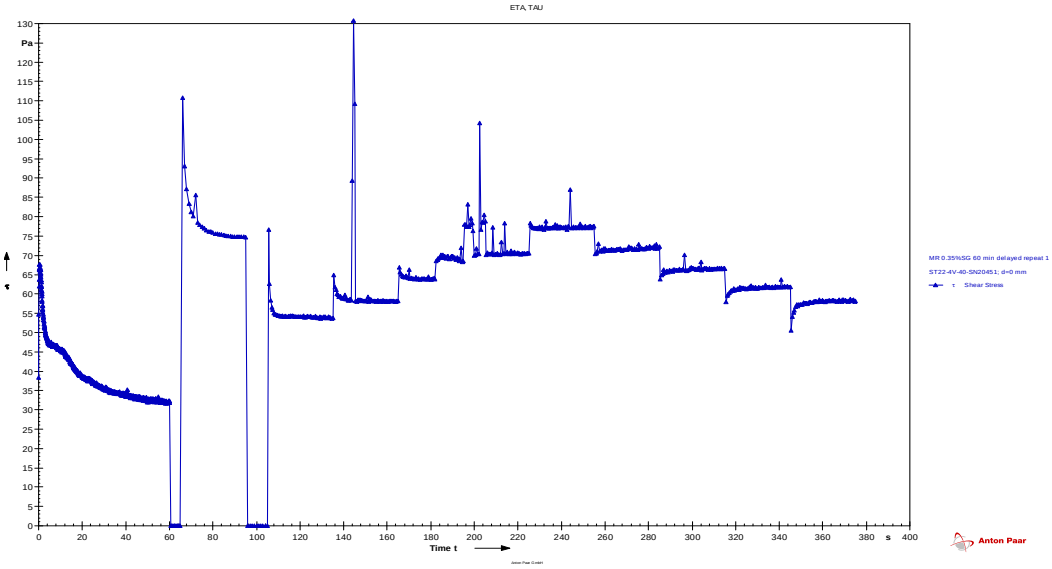

Figure A.20: Stress vs. time plot for the paste with delayed addition of 0.35% sodium gluconate at 60 minutes

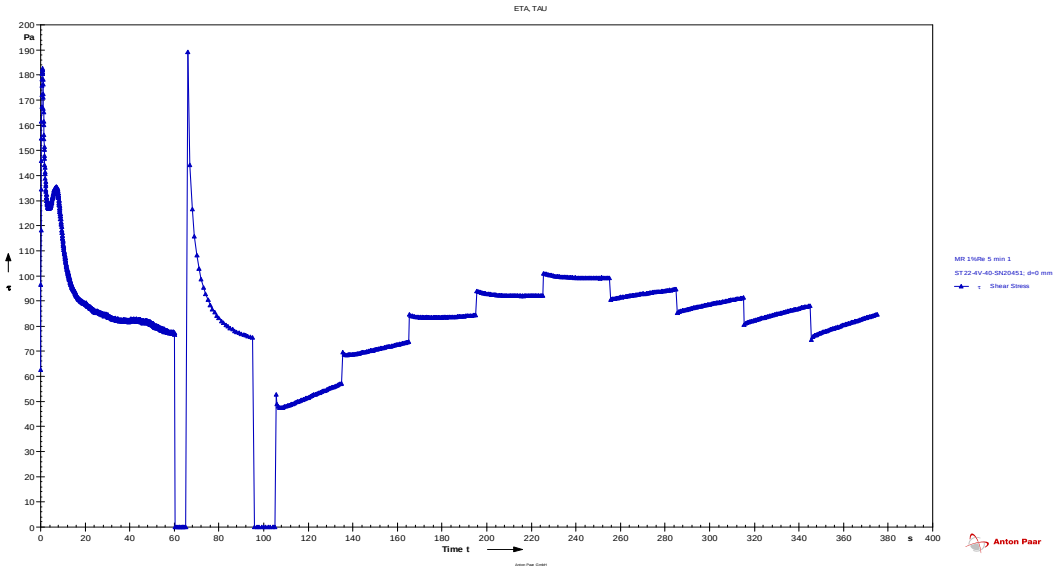

Figure A.21: Stress vs. time plot for the paste with 1.00% Recover at 5 minutes

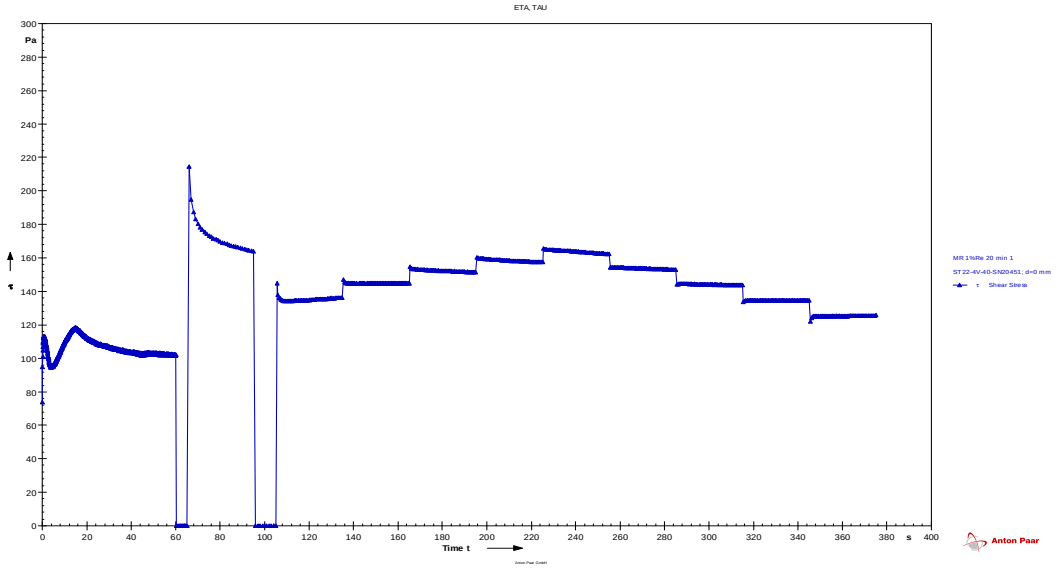

Figure A.22: Stress vs. time plot for the paste with 1.00% Recover at 20 minutes

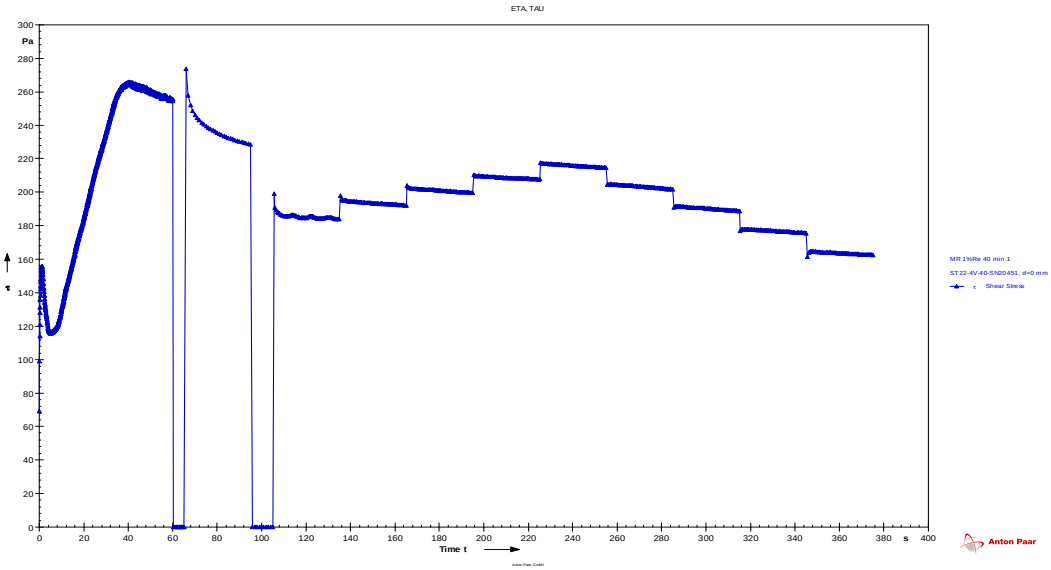

Figure A.23: Stress vs. time plot for the paste with 1.00% Recover at 40 minutes

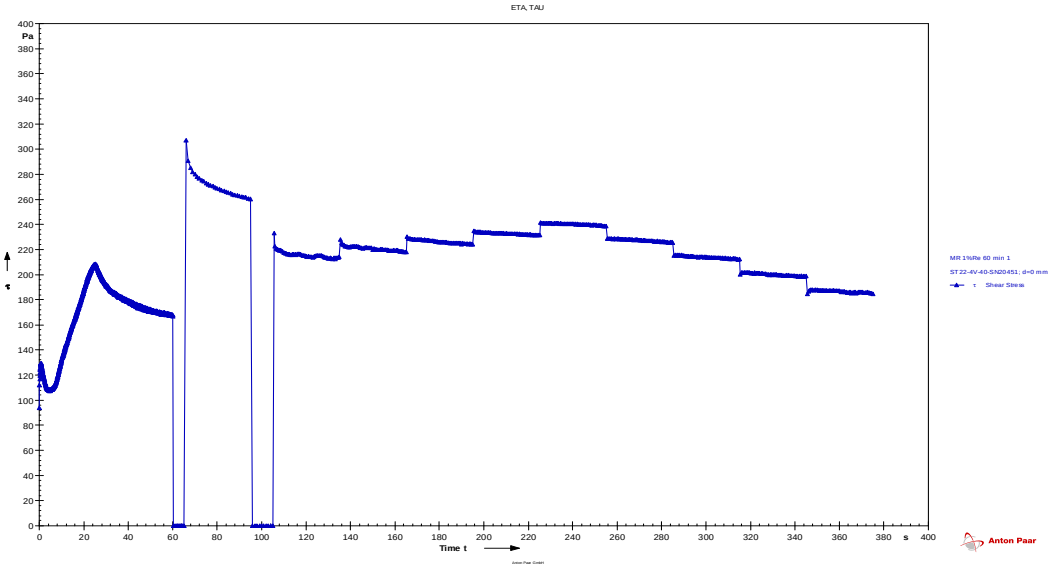

Figure A.24: Stress vs. time plot for the paste with 1.00% Recover at 60 minutes

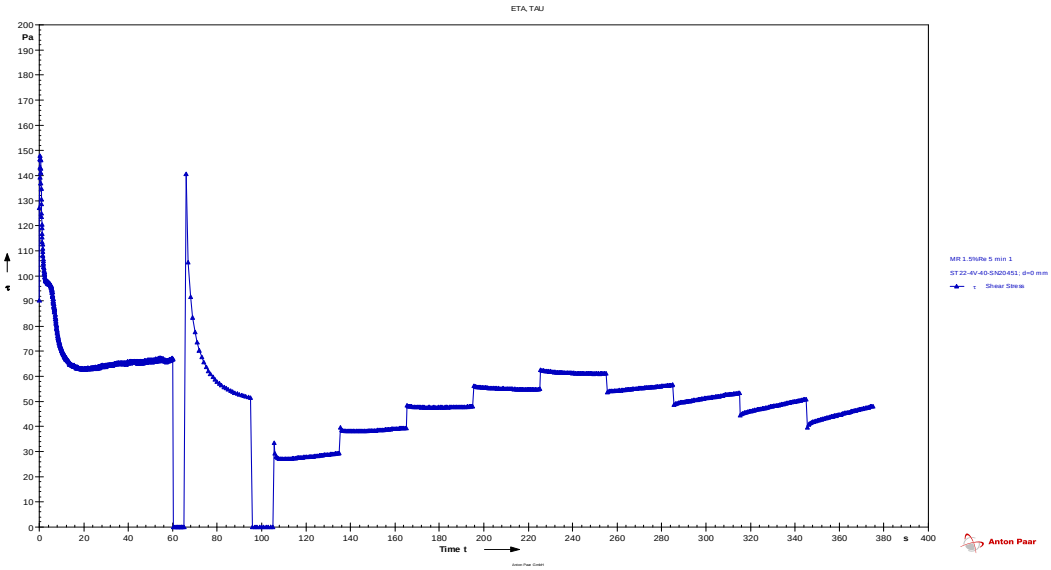

Figure A.25: Stress vs. time plot for the paste with 1.50% Recover at 5 minutes

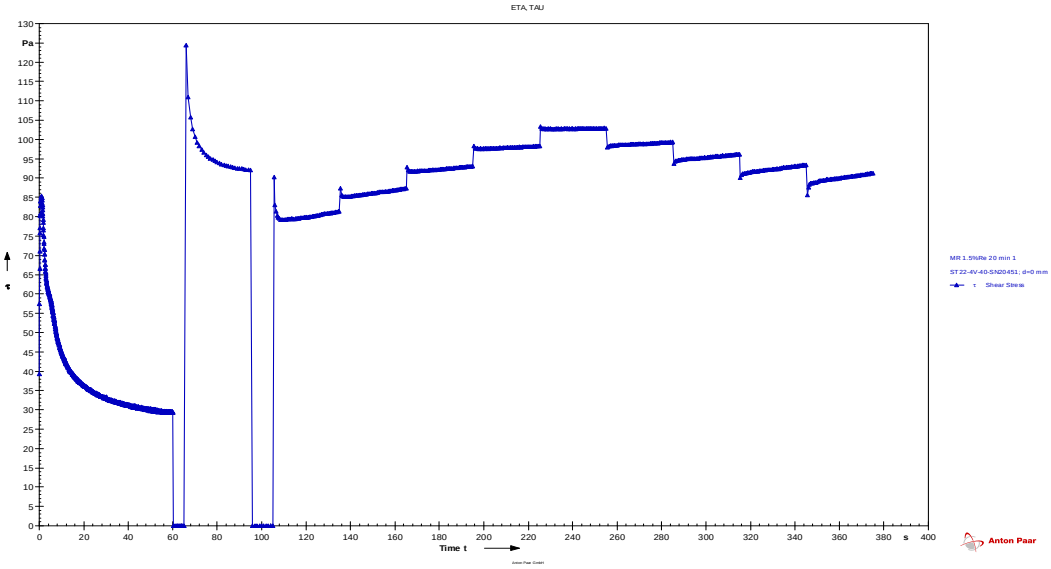

Figure A.26: Stress vs. time plot for the paste with 1.50% Recover at 20 minutes

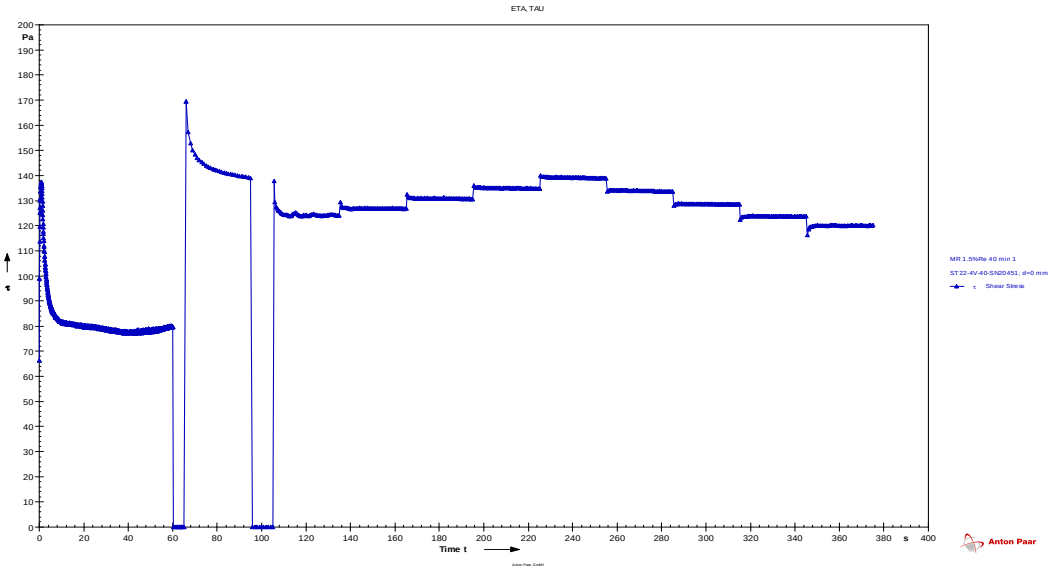

Figure A.27: Stress vs. time plot for the paste with 1.50% Recover at 40 minutes

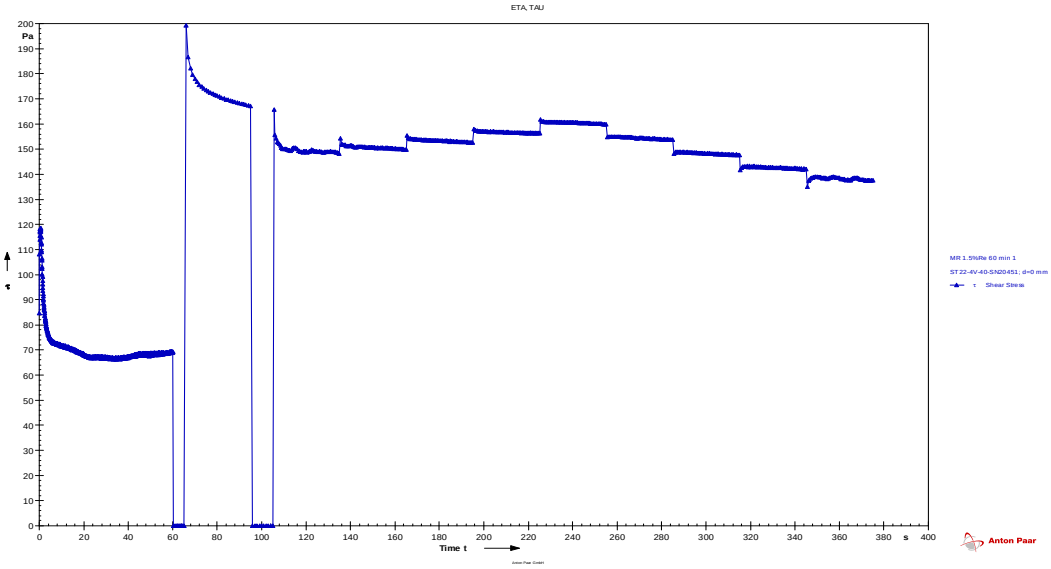

Figure A.28: Stress vs. time plot for the paste with 1.50% Recover at 60 minutes

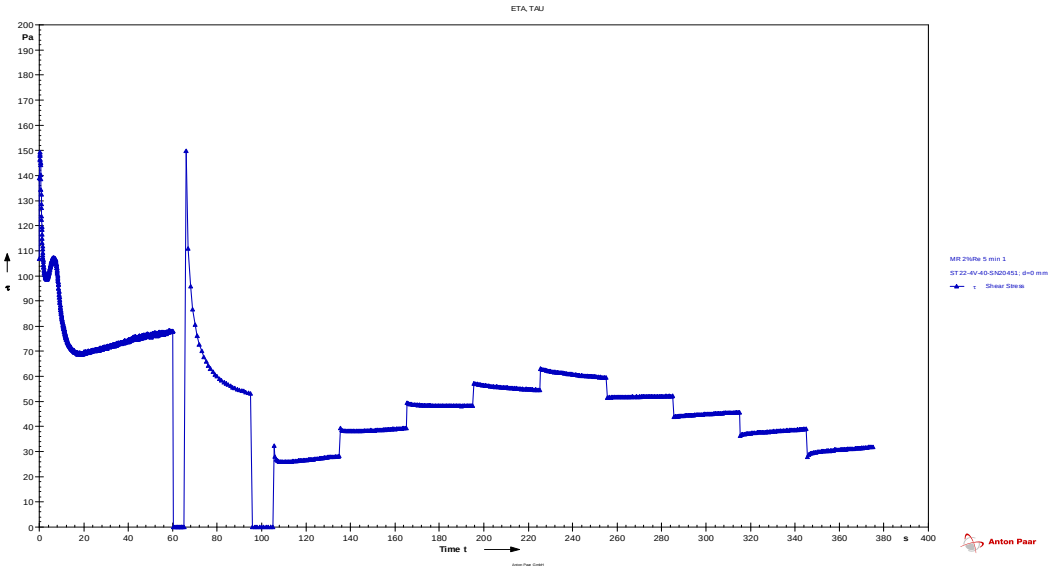

Figure A.29: Stress vs. time plot for the paste with 2.00% Recover at 5 minutes

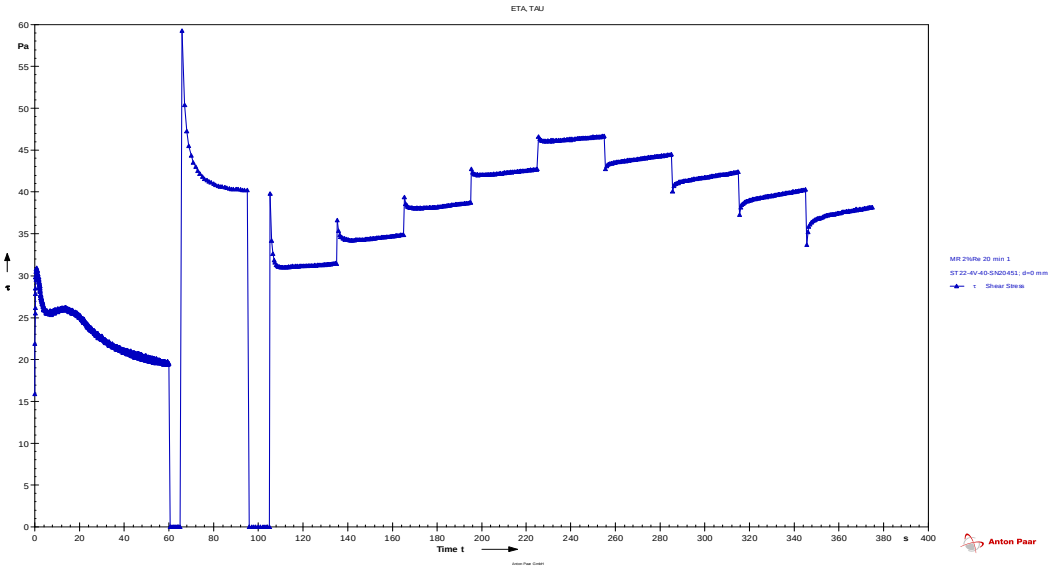

Figure A.30: Stress vs. time plot for the paste with 2.00% Recover at 20 minutes

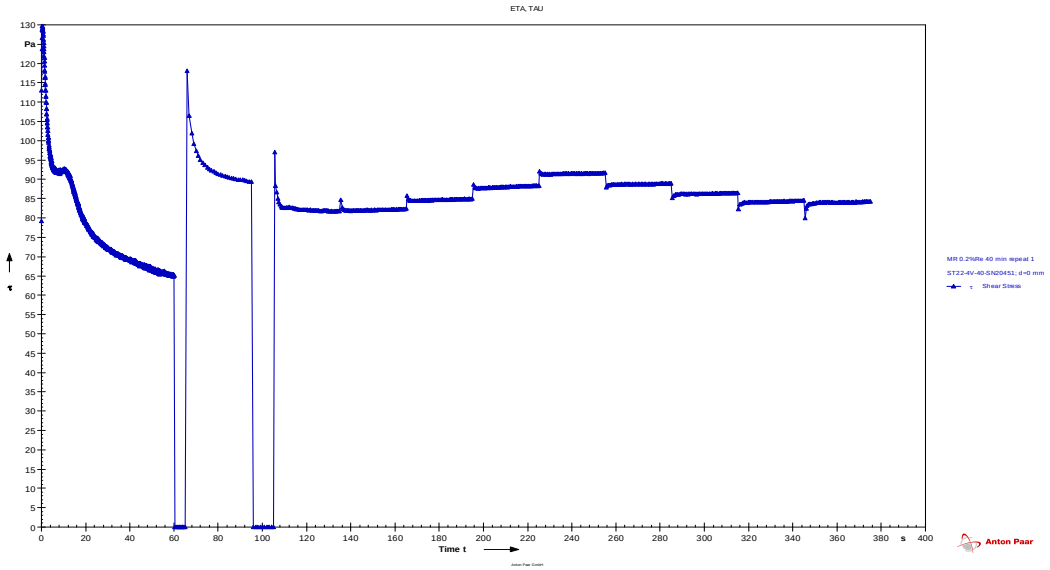

Figure A.31: Stress vs. time plot for the paste with 2.00% Recover at 40 minutes

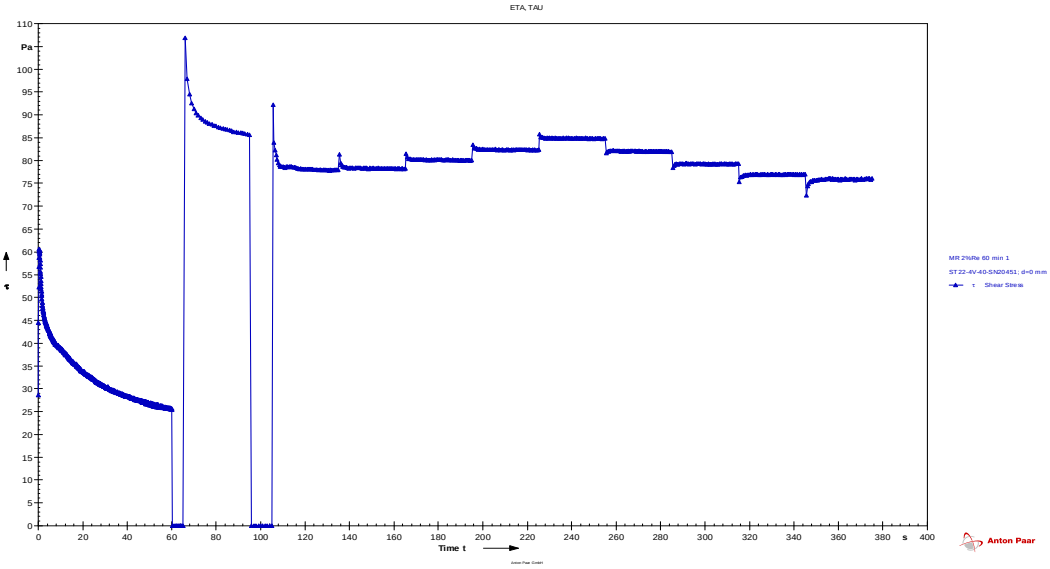

Figure A.32: Stress vs. time plot for the paste with 2.00% Recover at 60 minutes

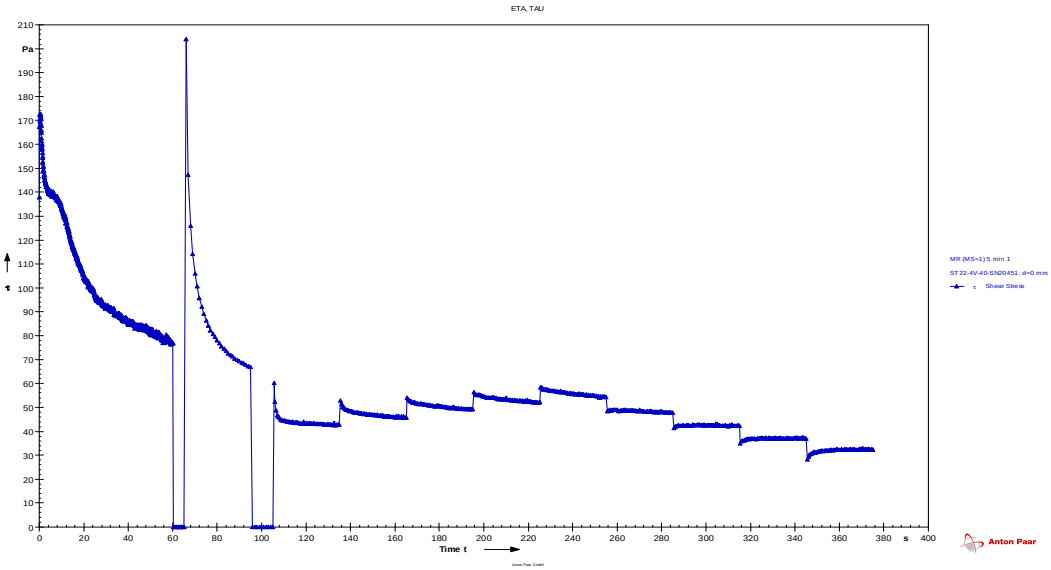

Figure A.33: Stress vs. time plot for the paste with fumed silica addition at 5 minutes

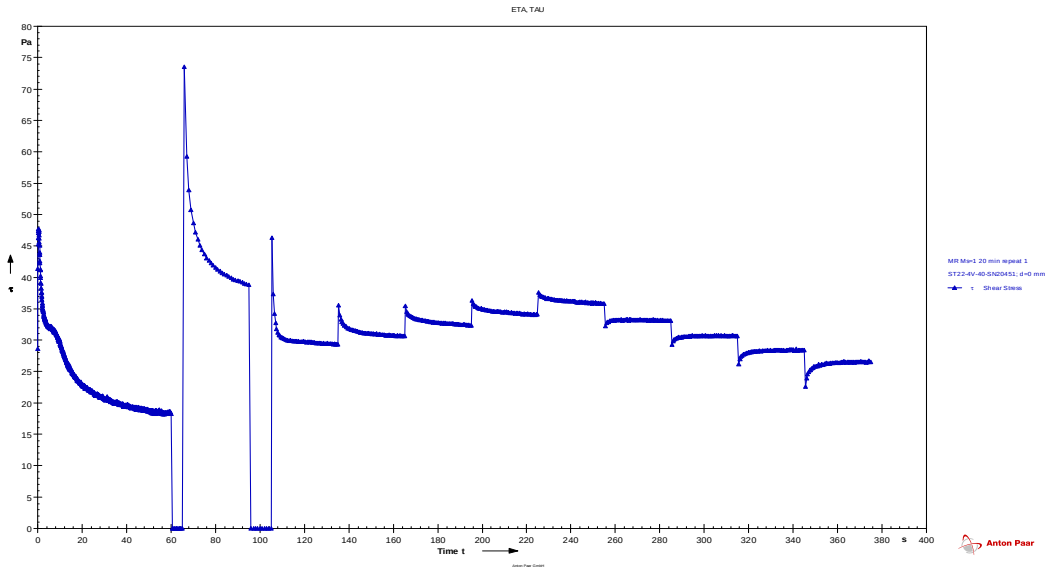

Figure A.34: Stress vs. time plot for the paste with fumed silica addition at 20 minutes

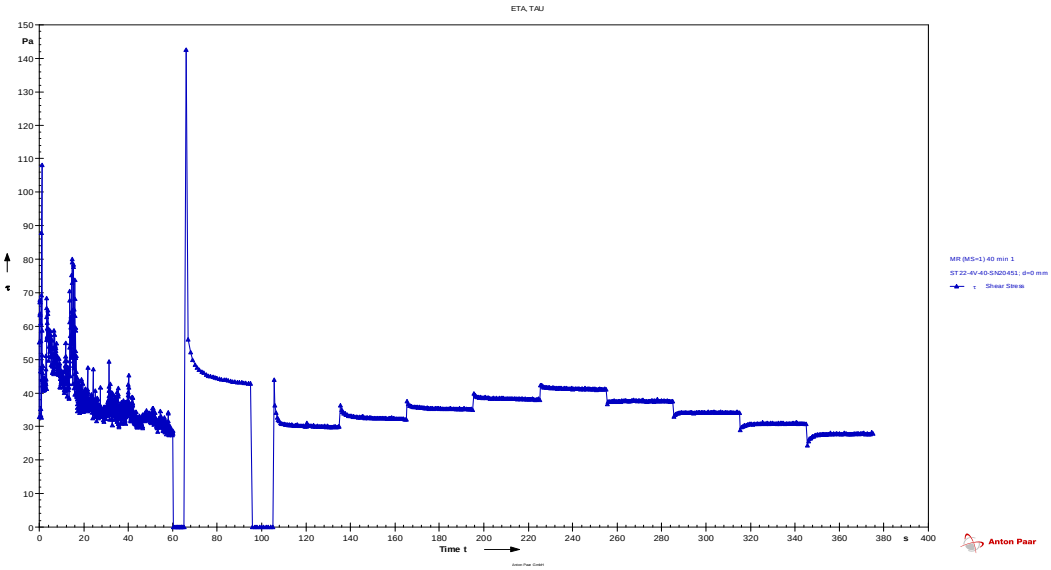

Figure A.35: Stress vs. time plot for the paste with fumed silica addition at 40 minutes

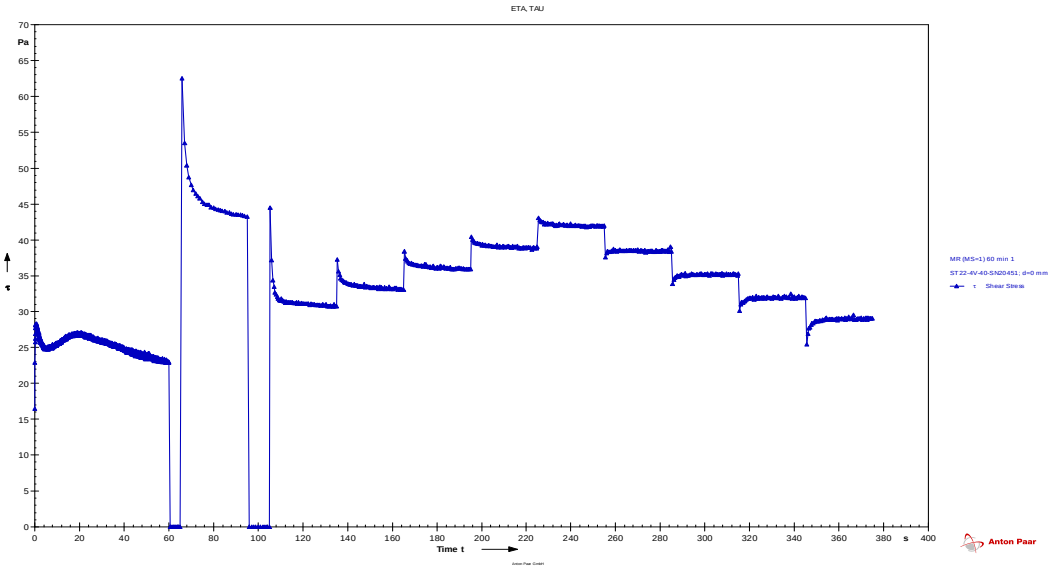

Figure A.36: Stress vs. time plot for the paste with fumed silica addition at 60 minutes

Appendix B: Flow Curves of MR Fly Ash Geopolymer Pastes

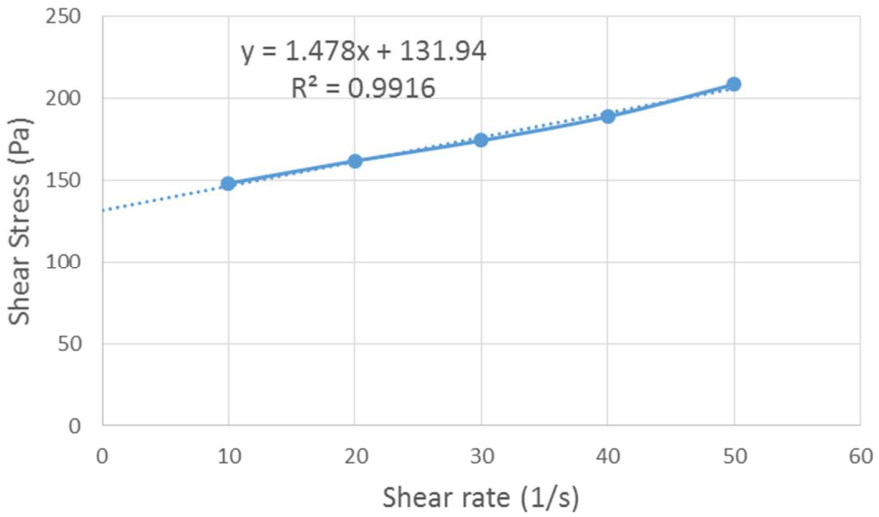

Figure B.1: Flow curve for geopolymer paste with 0.25% sodium gluconate at 5 minutes

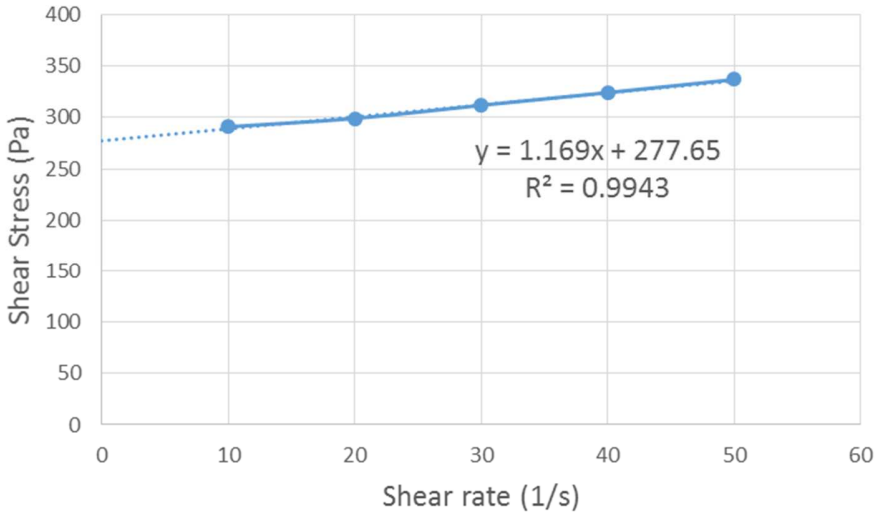

Figure B.2: Flow curve for geopolymer paste with 0.25% sodium gluconate at 20 minutes

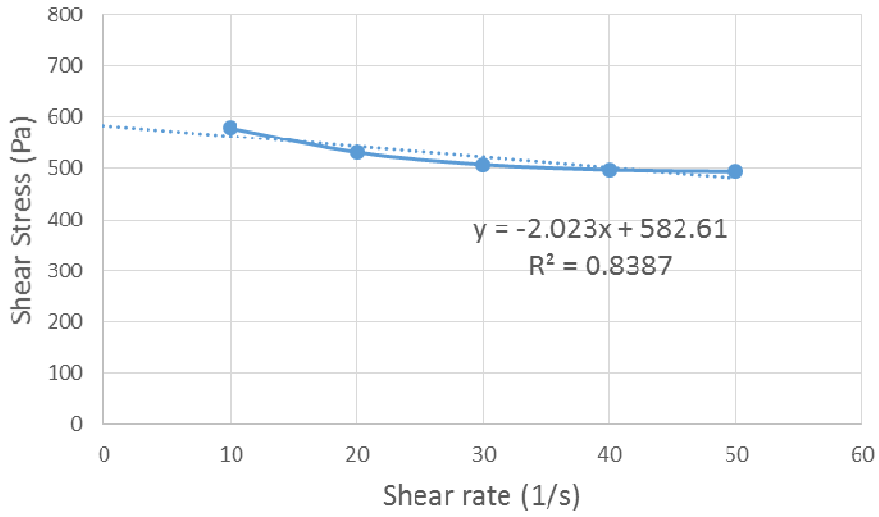

Figure B.3: Flow curve for geopolymer paste with 0.25% sodium gluconate at 40 minutes

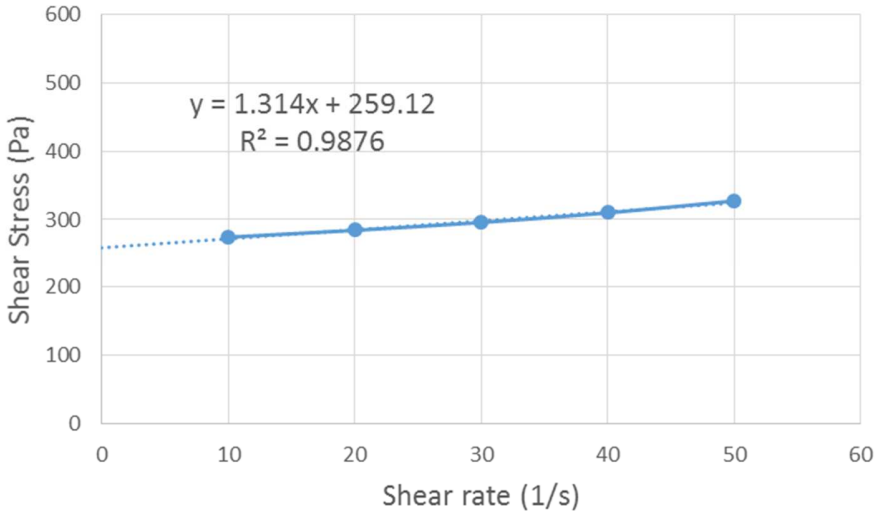

Figure B.4: Flow curve for geopolymer paste with 0.25% sodium gluconate at 60 minutes

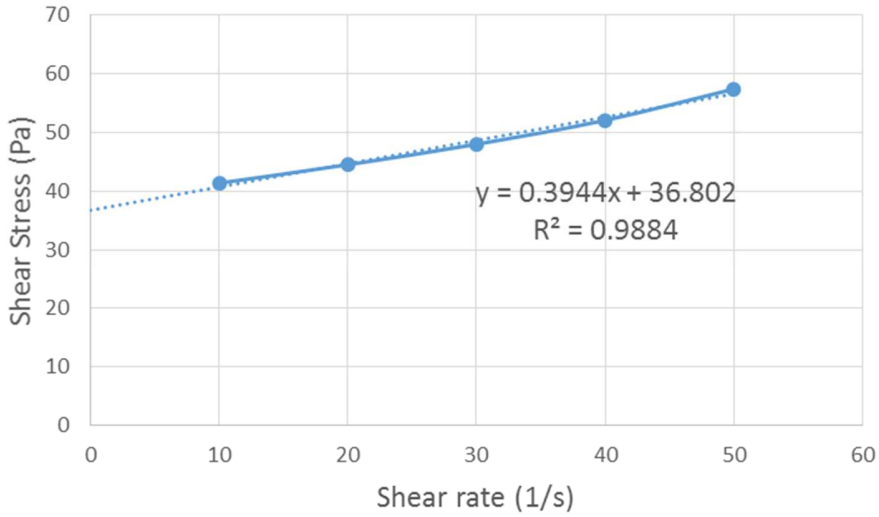

Figure B.5: Flow curve for geopolymer paste with 0.35% sodium gluconate at 5 minutes

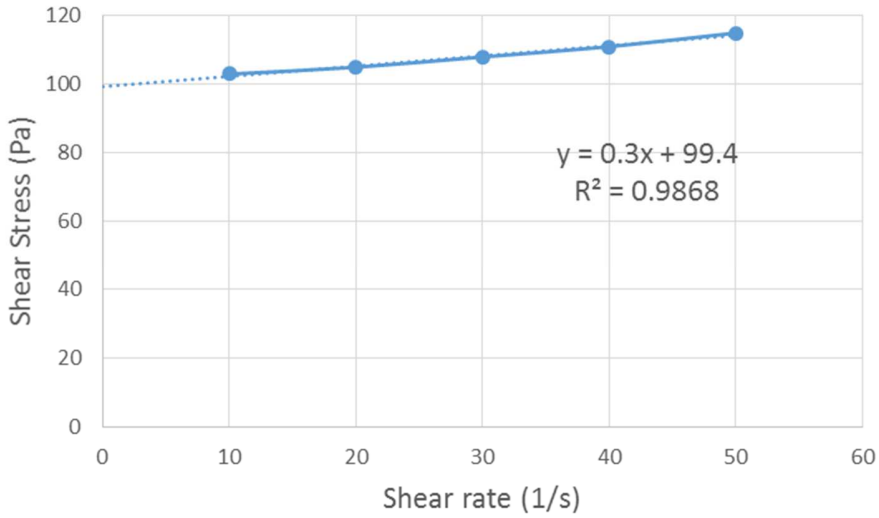

Figure B.6: Flow curve for geopolymer paste with 0.35% sodium gluconate at 20 minutes

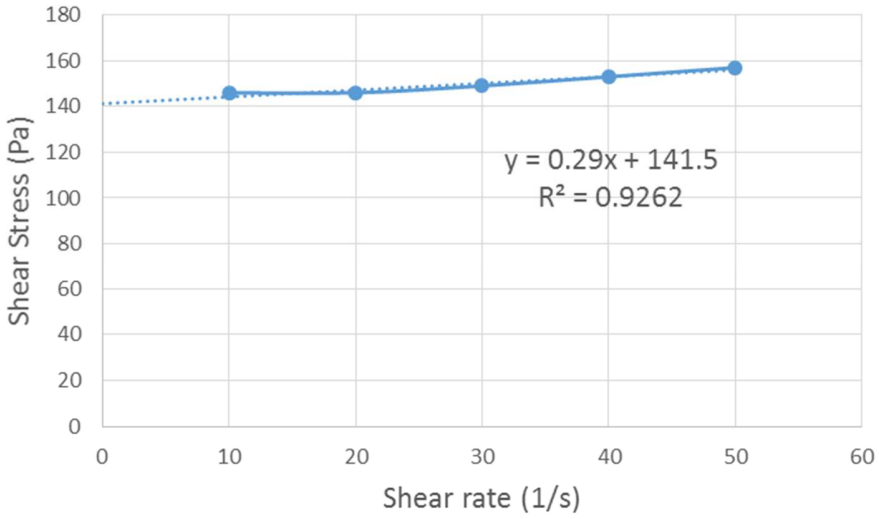

Figure B.7: Flow curve for geopolymer paste with 0.35% sodium gluconate at 40 minutes

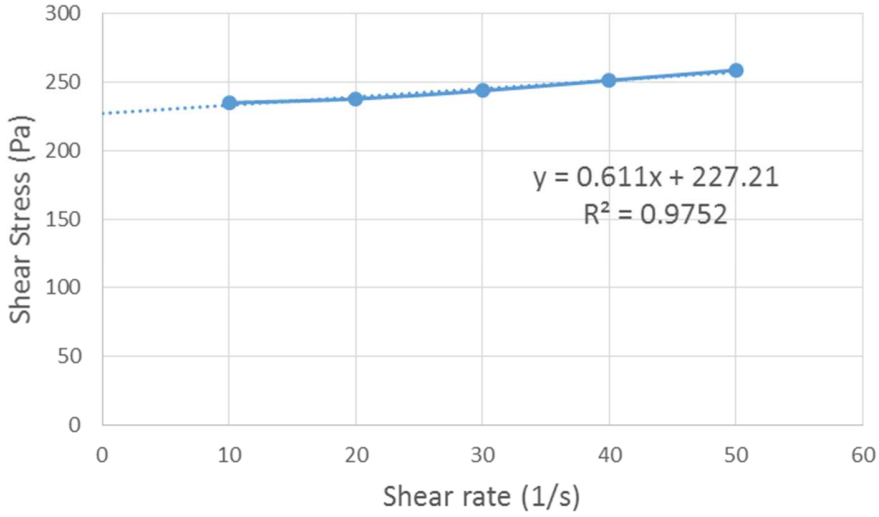

Figure B.8: Flow curve for geopolymer paste with 0.35% sodium gluconate at 60 minutes

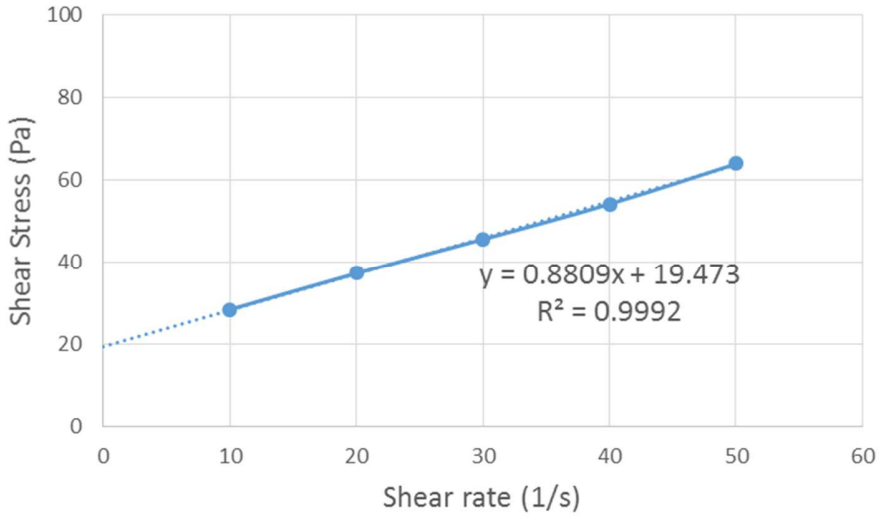

Figure B.9: Flow curve for geopolymer paste with 0.50% sodium gluconate at 5 minutes

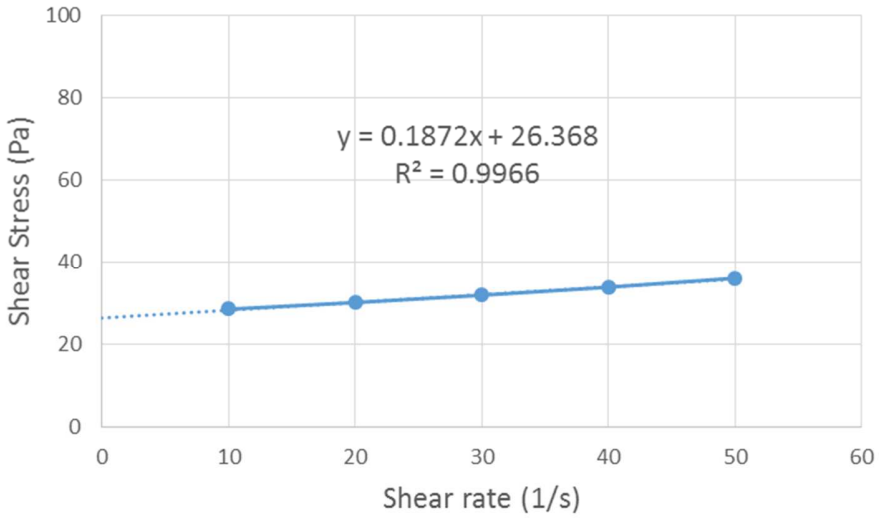

Figure B.10: Flow curve for geopolymer paste with 0.50% sodium gluconate at 20 minutes

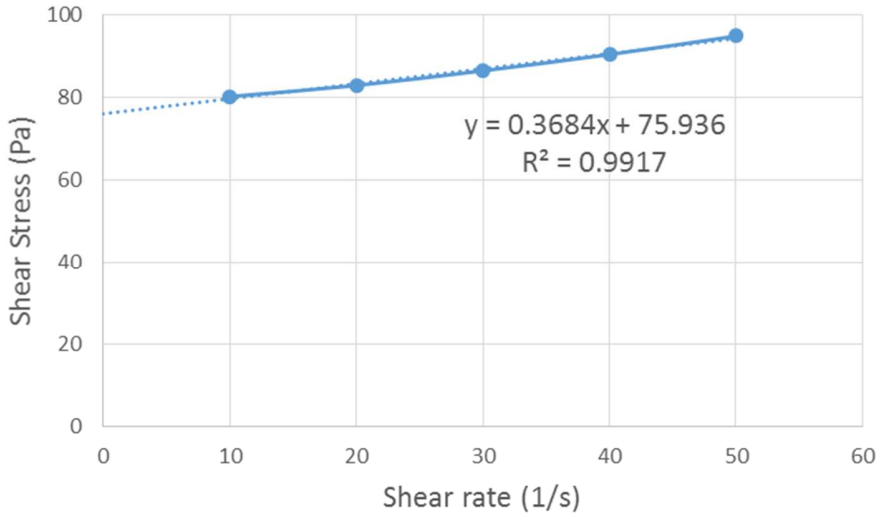

Figure B.11: Flow curve for geopolymer paste with 0.50% sodium gluconate at 40 minutes

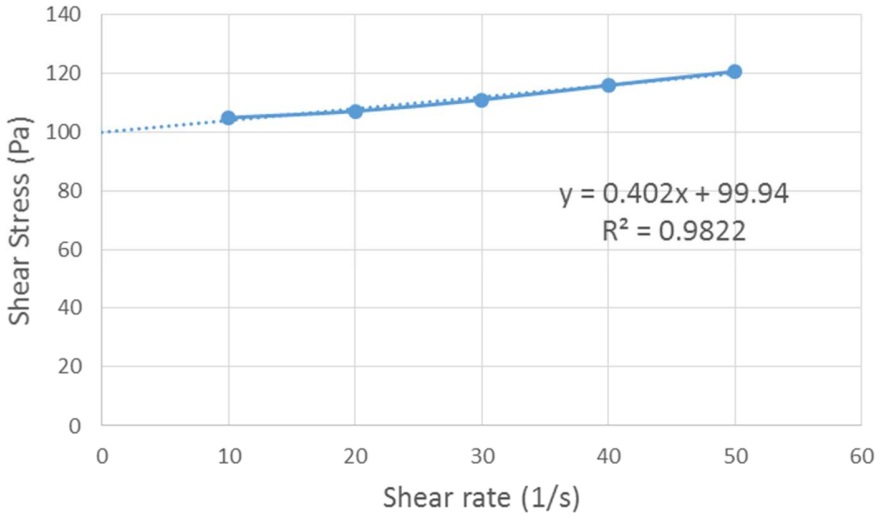

Figure B.12: Flow curve for geopolymer paste with 0.50% sodium gluconate at 60 minutes

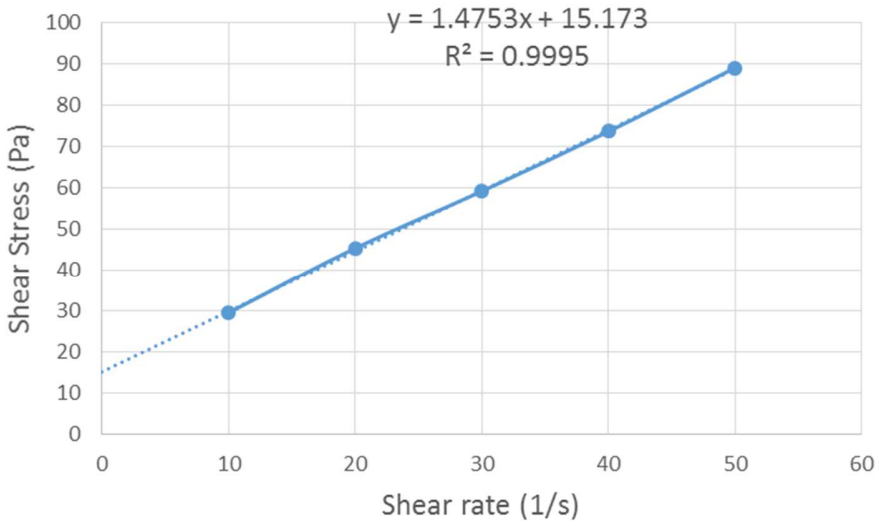

Figure B.13: Flow curve for geopolymer paste with delayed addition of 0.25% sodium gluconate at 5 minutes

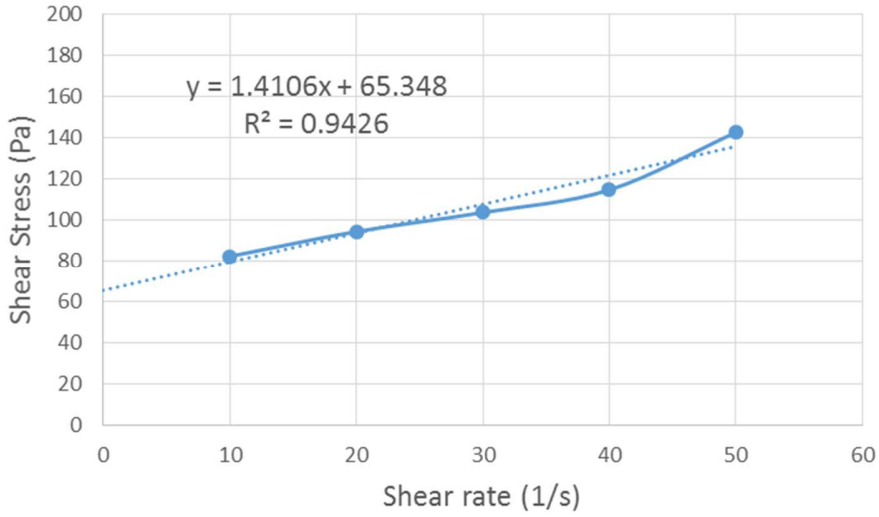

Figure B.14: Flow curve for geopolymer paste with delayed addition of 0.25% sodium gluconate at 20 minutes

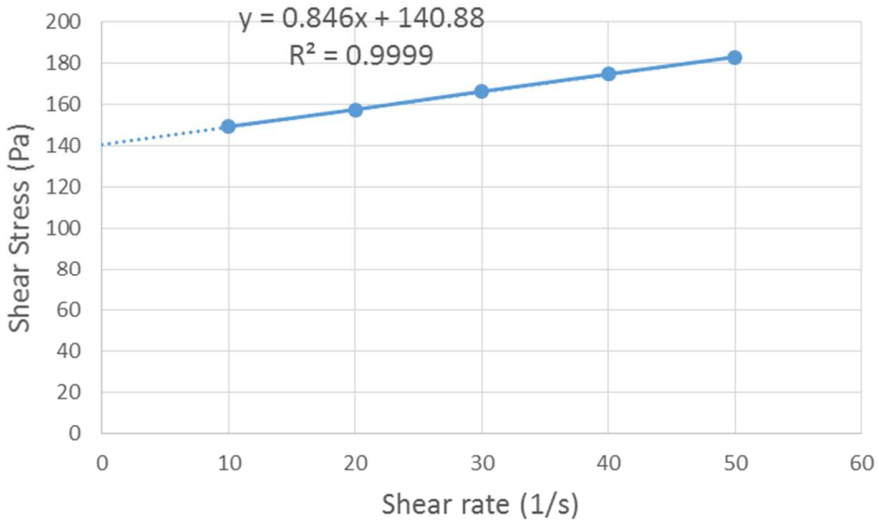

Figure B.15: Flow curve for geopolymer paste with delayed addition of 0.25% sodium gluconate at 40 minutes

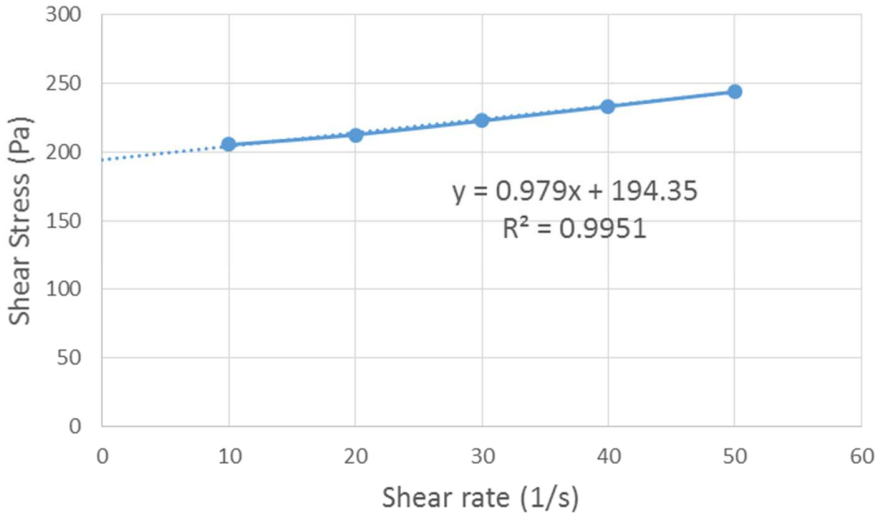

Figure B.16: Flow curve for geopolymer paste with delayed addition of 0.25% sodium gluconate at 60 minutes

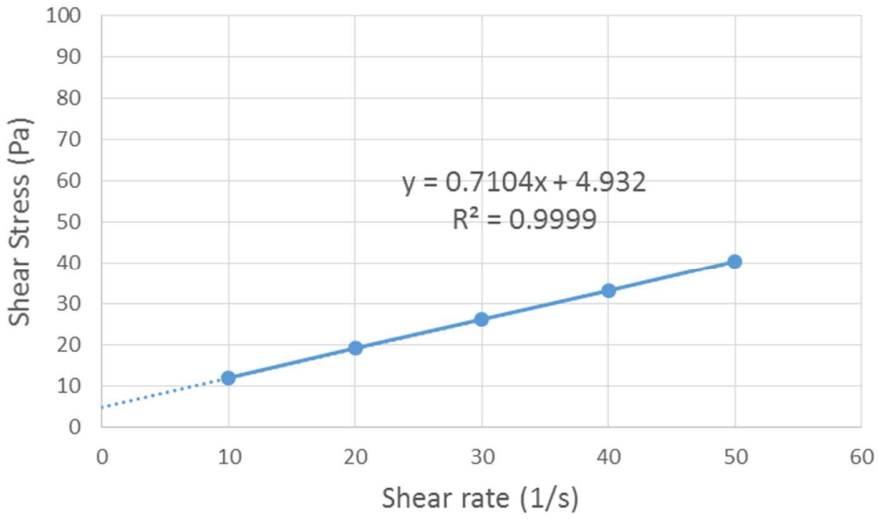

Figure B.17: Flow curve for geopolymer paste with delayed addition of 0.35% sodium gluconate at 5 minutes

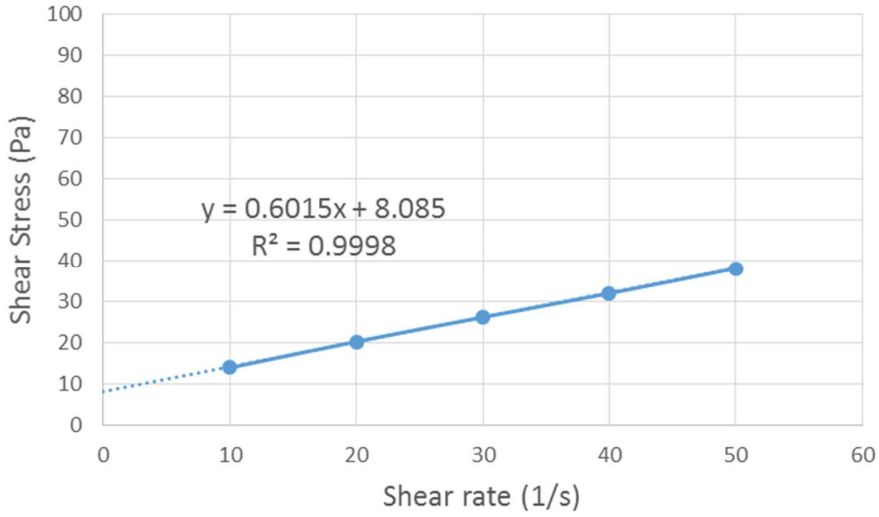

Figure B.18: Flow curve for geopolymer paste with delayed addition of 0.35% sodium gluconate at 20 minutes

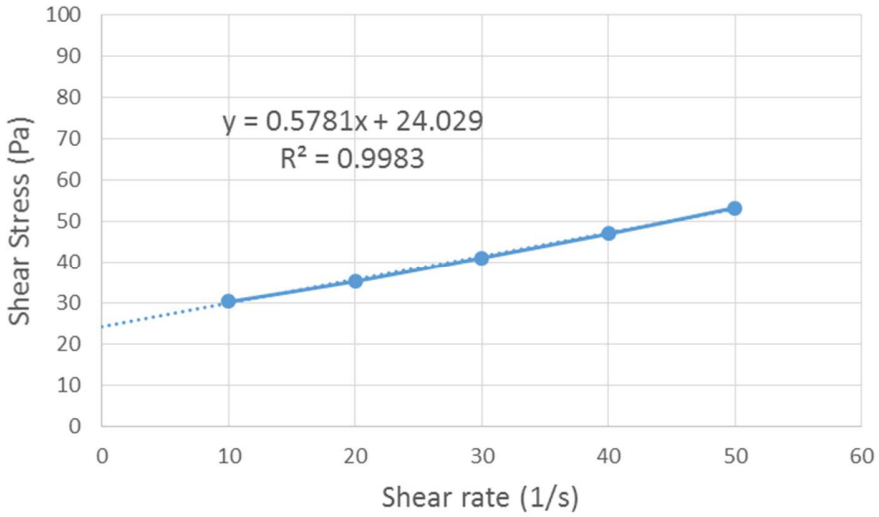

Figure B.19: Flow curve for geopolymer paste with delayed addition of 0.35% sodium gluconate at 40 minutes

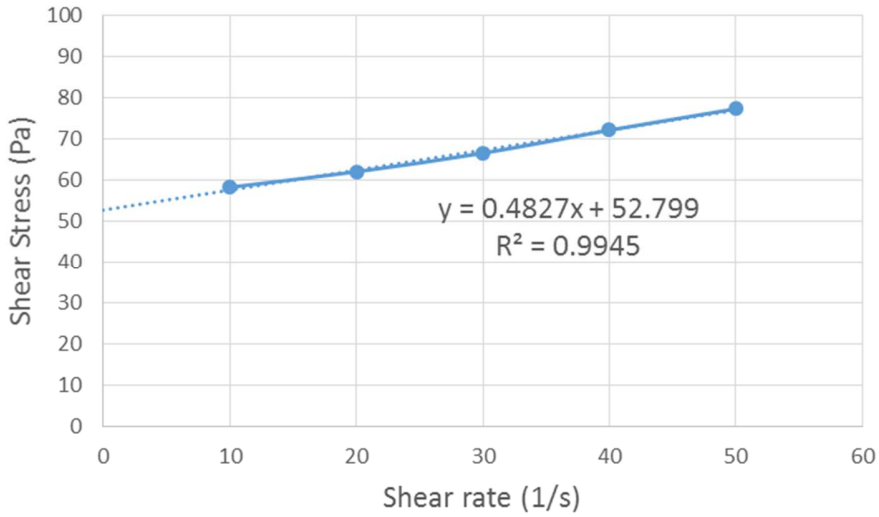

Figure B.20: Flow curve for geopolymer paste with delayed addition of 0.35% sodium gluconate at 60 minutes

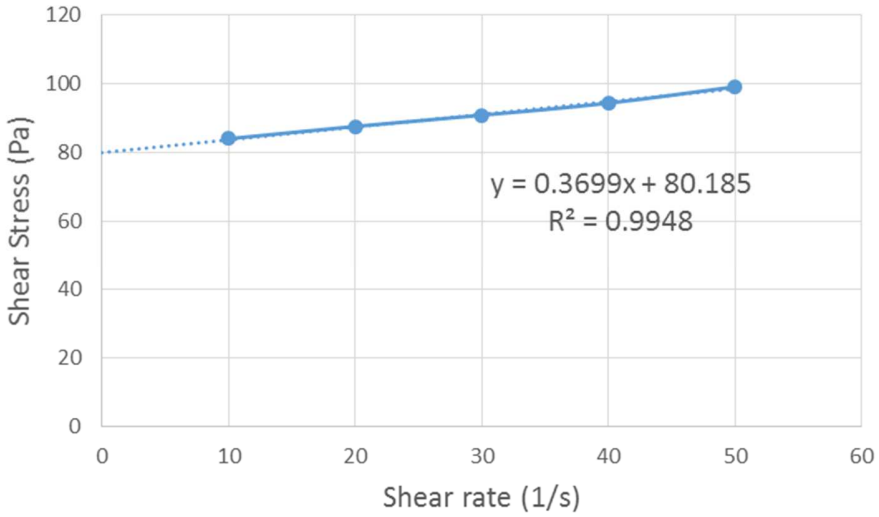

Figure B.21: Flow curve for geopolymer paste with 1.00% Recover at 5 minutes

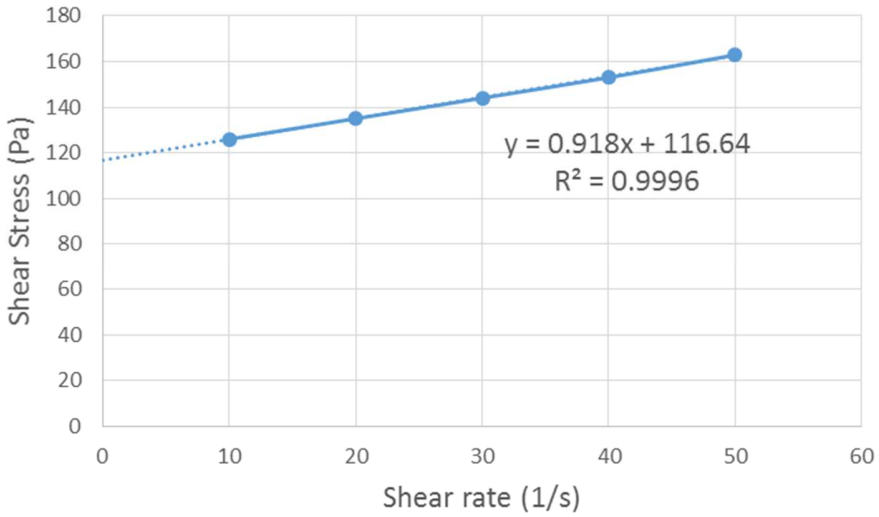

Figure B.22: Flow curve for geopolymer paste with 1.00% Recover at 20 minutes

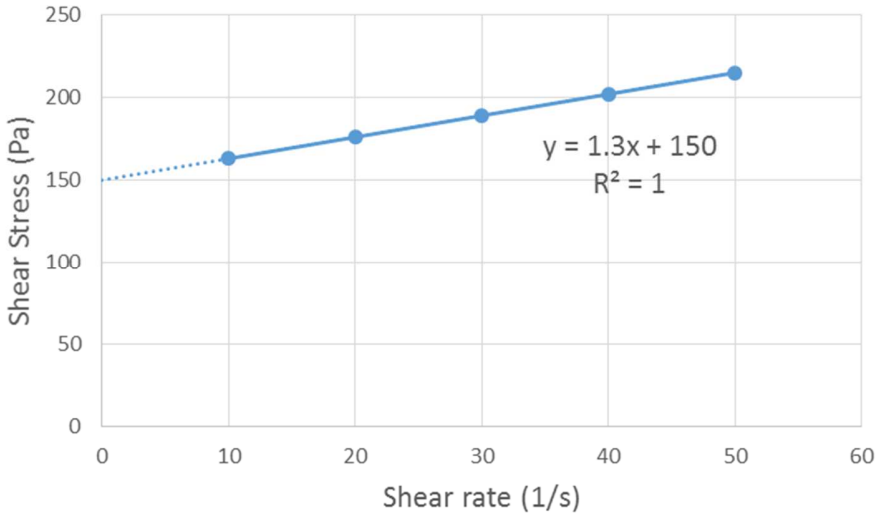

Figure B.23: Flow curve for geopolymer paste with 1.00% Recover at 40 minutes

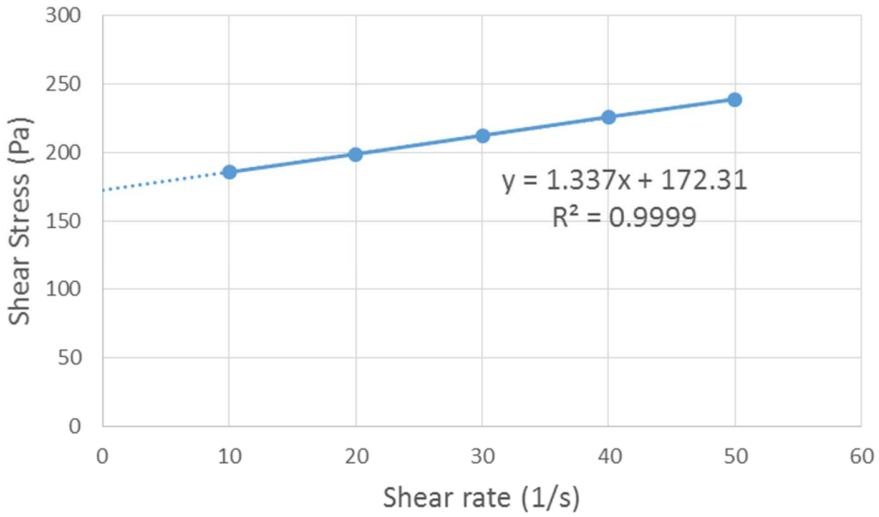

Figure B.24: Flow curve for geopolymer paste with 1.00% Recover at 60 minutes

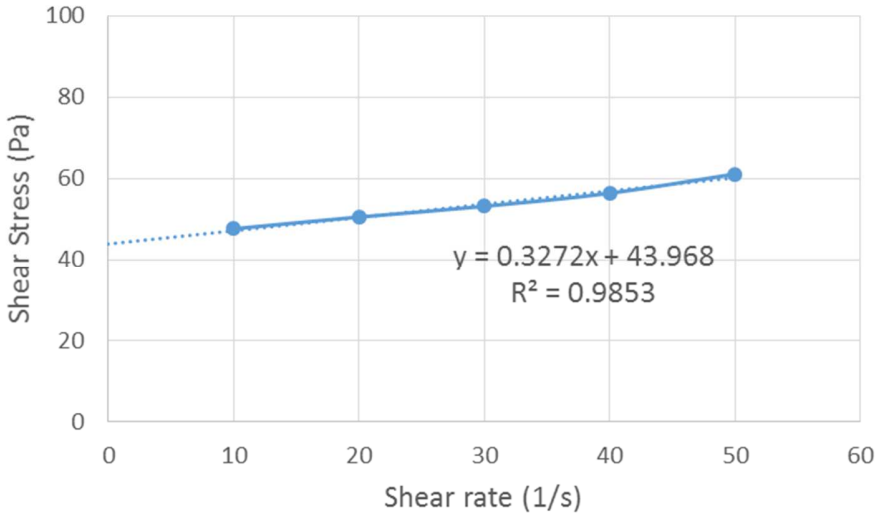

Figure B.25: Flow curve for geopolymer paste with 1.50% Recover at 5 minutes

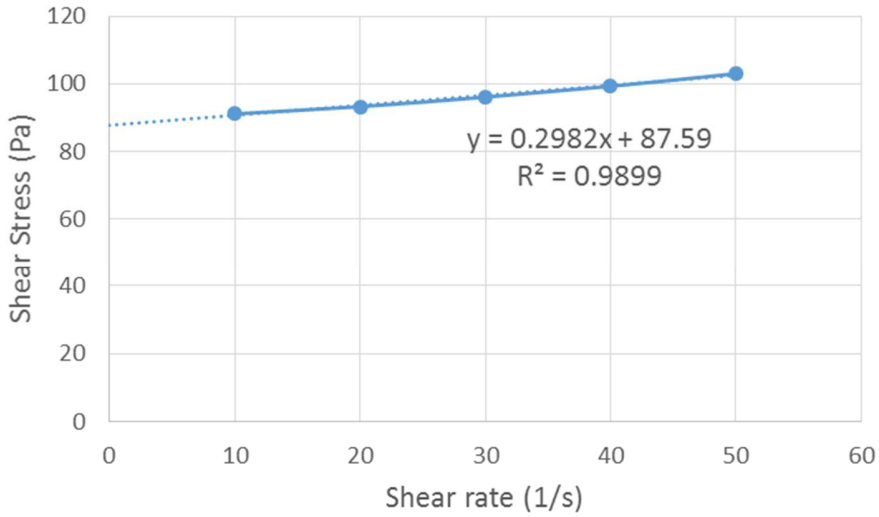

Figure B.26: Flow curve for geopolymer paste with 1.50% Recover at 20 minutes

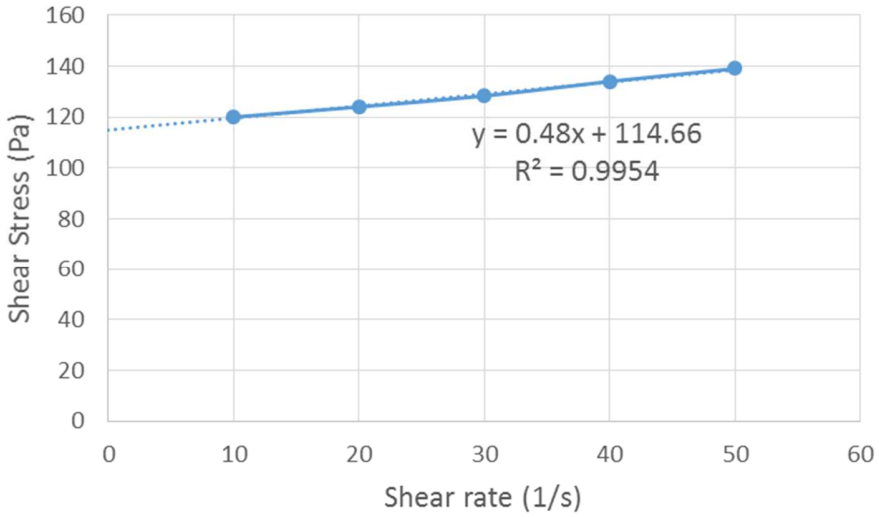

Figure B.27: Flow curve for geopolymer paste with 1.50% Recover at 40 minutes

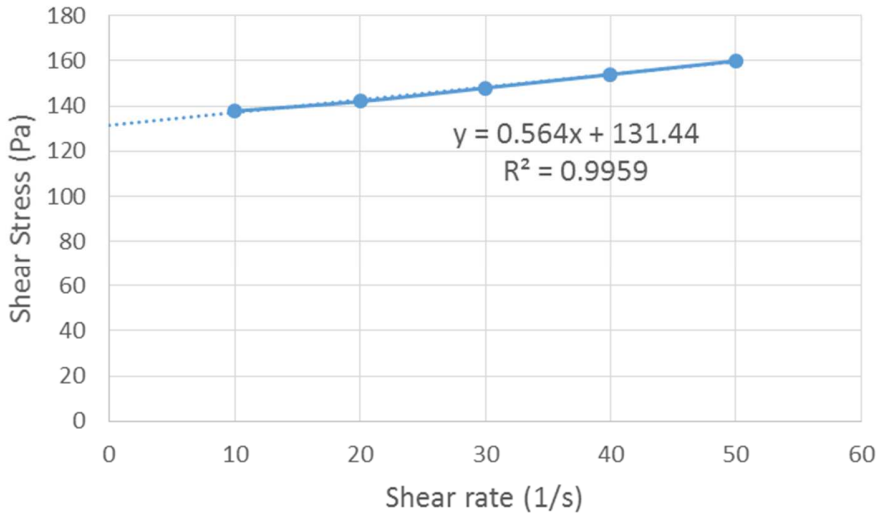

Figure B.28: Flow curve for geopolymer paste with 1.50% Recover at 60 minutes

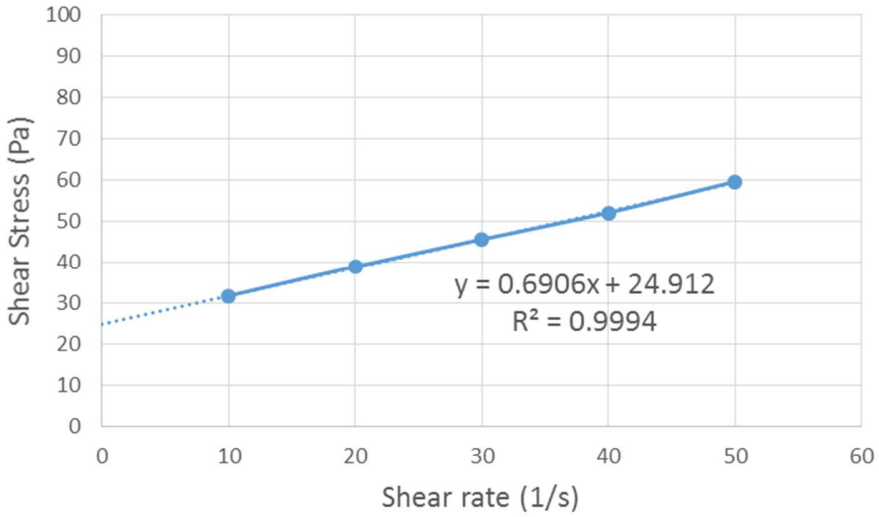

Figure B.29: Flow curve for geopolymer paste with 2.00% Recover at 5 minutes

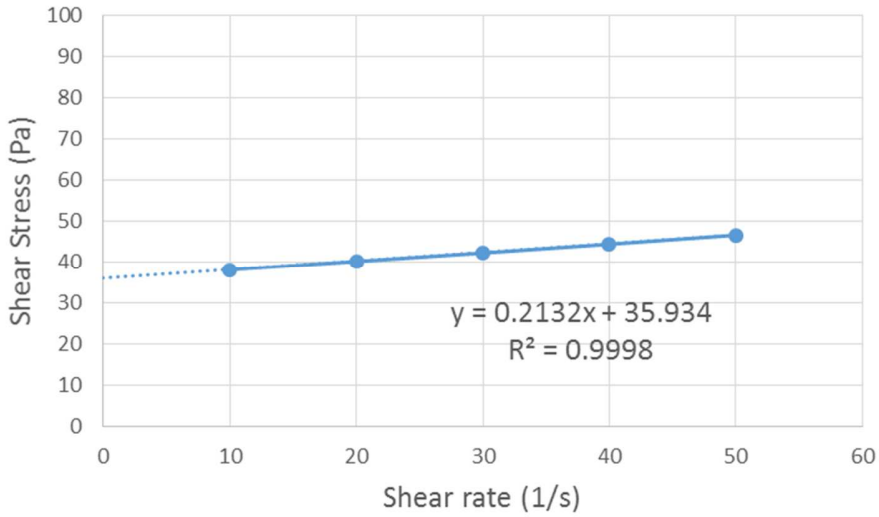

Figure B.30: Flow curve for geopolymer paste with 2.00% Recover at 20 minutes

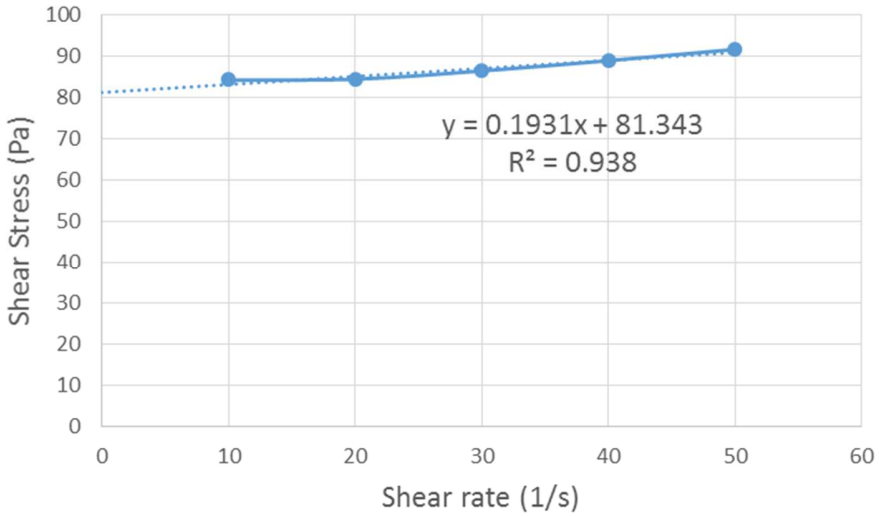

Figure B.31: Flow curve for geopolymer paste with 2.00% Recover at 40 minutes

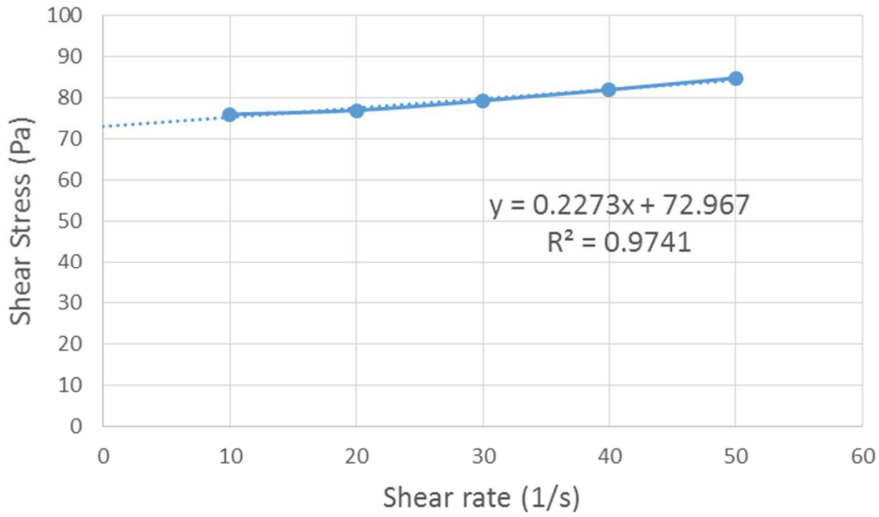

Figure B.32: Flow curve for geopolymer paste with 2.00% Recover at 60 minutes

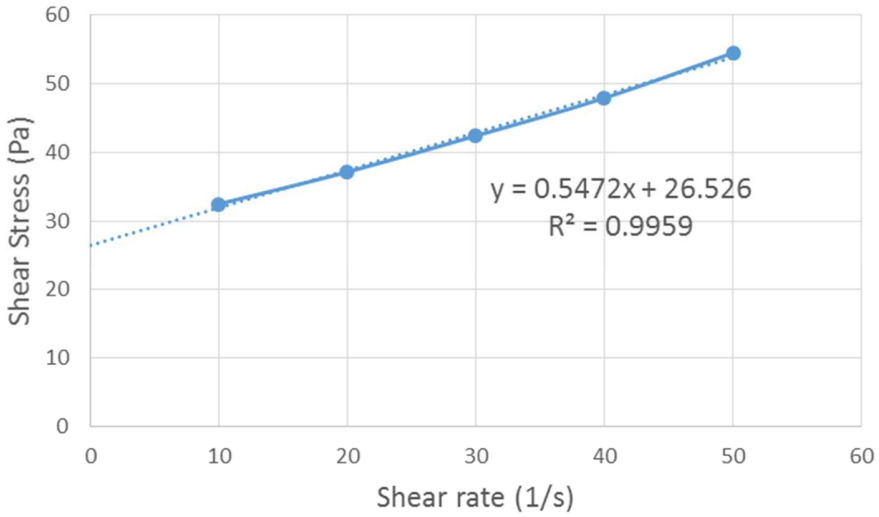

Figure B.33: Flow curve for geopolymer paste with fumed silica addition at 5 minutes

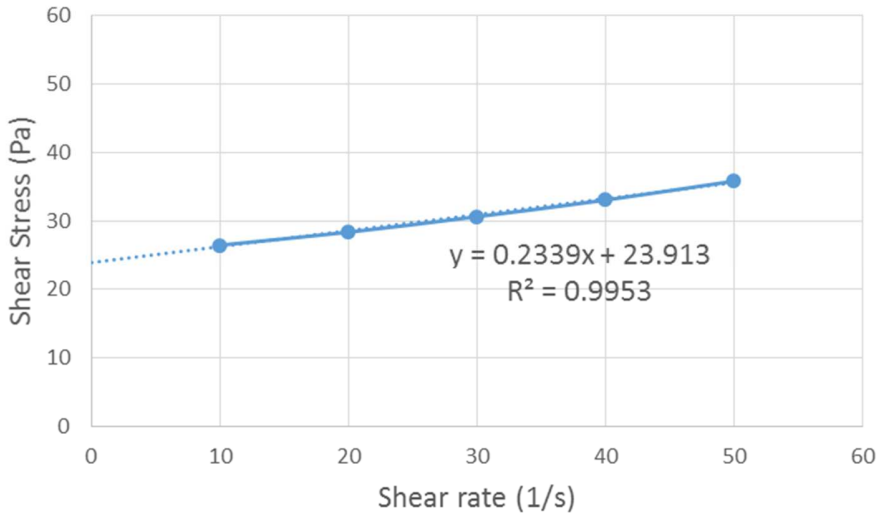

Figure B.34: Flow curve for geopolymer paste with fumed silica addition at 20 minutes

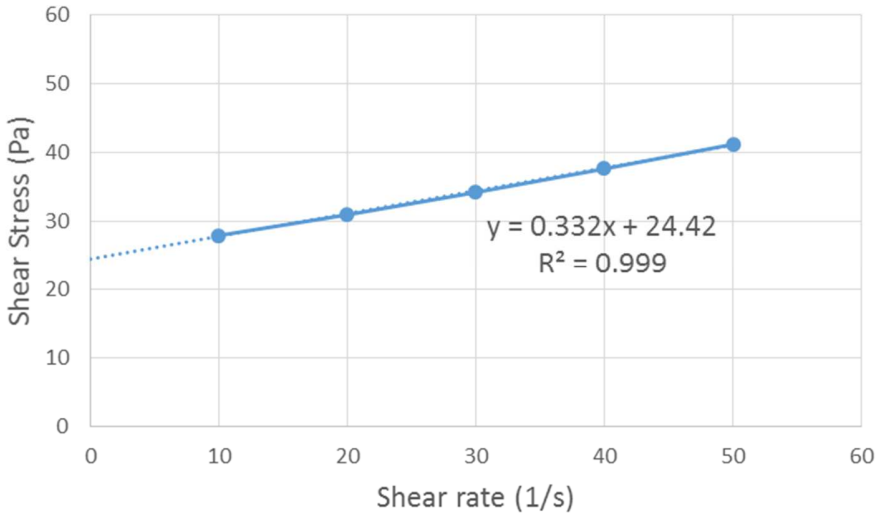

Figure B.35: Flow curve for geopolymer paste with fumed silica addition at 40 minutes

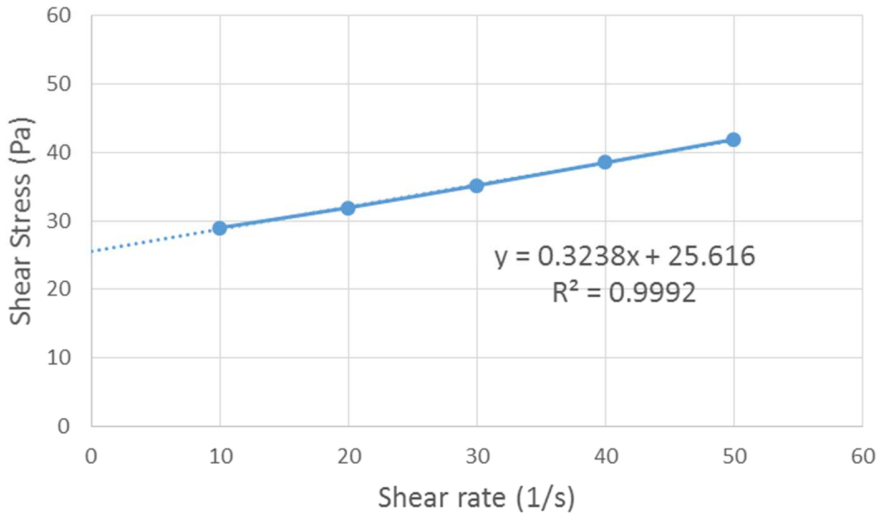

Figure B.36: Flow curve for geopolymer paste with fumed silica addition at 60 minutes

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